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 Anales de la Real Sociedad Española de Física y Química, Serie B.
 Anales de la Sociedad de Biología de Bogotá.
 Anales de la Sociedad Científica Argentina.
 Analyst.
 Analytica Chimica Acta.
 Analytical Chemistry.
 Angewandte Chemie.
 Annales d'Endocrinologie [Paris].
 Annales des Falsifications et des Fraudes.
 Annales de l'Institut Pasteur.
 Annales Pharmaceutiques Françaises.
 Annales Universitatis Mariae Curie-Skłodowska.
 Annali di Chimica [Rome].
 Annali della Sperimentazione Agraria [Rome].
 Annual Report of Takamine Laboratory.
 Antibiotics and Chemotherapy.
 Antibiotiki.
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 Applied Spectroscopy.
 Aptechnoe Delo.
 Archiv für das Eisenhüttenwesen.
 Archiv der Pharmazie [Berlin].
 Archives of Biochemistry and Biophysics.
 Arquivos de Bromatologia [Rio de Janeiro].
 Arzneimittel-Forschung.
 Atomic Energy Research Establishment Reports [U.K.].
 Atomics.
 Australasian Journal of Pharmacy.
 Australian Journal of Applied Science.
 Australian Journal of Biological Sciences.
 Australian Journal of Instrument Technology.

 Berichte der deutschen keramischen Gesellschaft.
 Berichte des Ohara Instituts für landwirtschaftliche Biologie, Okayama Universität.
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 Biochemische Zeitschrift.
 Biochimica et Biophysica Acta.
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 Brauwelt, B.

JOURNALS

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 British Medical Journal.
 British Standards Institution. Standards.
 Bulletin de l'Académie Polonaise des Sciences.
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Canadian Dairy and Ice Cream Journal.
 Canadian Journal of Biochemistry and Physiology.
 Canadian Journal of Chemistry.
 Canadian Journal of Technology.
 Časopis Lékáru Českých.
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 Cereal Science Today.
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 Collection of Czechoslovak Chemical Communications.
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 Contributions. Boyce Thompson Institute for Plant Research.
 Croatica Chemica Acta.

Dansk Tidsskrift for Farmaci.
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Fuel [London].

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Gazzetta Chimica Italiana.
General Electric Co., Ltd., Journal.
Geochimica et Cosmochimica Acta.
Gigiena i Sanitariya.
Glas-Email-Keramo-Technik.
Glass Industry.
Grasas y Aceites [Seville].
Guy's Hospital Reports.

Helvetica Chimica Acta.
Hilger Journal.
Hoppe-Seyler's Zeitschrift für Physiologische Chemie.
Hormel Institute of the University of Minnesota Annual Report.

Indian Journal of Pharmacy.
Industria y Química.
Industrial Chemist and Chemical Manufacturer.
Industrie Chimique Belge.
Industrie de la Parfumerie.
Información de Química Analítica.
Institute of the Rubber Industry Transactions.
Instituto del Hierro y del Acero.
International Sugar Journal.
Iowa State College Journal of Science.
Izvestiya Akademii Nauk SSSR Otdelenie Khimicheskikh Nauk.
Izvestiya Akademii Nauk SSSR Seriya Fizicheskaya.

"J. Stefan" Institute Reports [Ljubljana].
Japan Analyst.
Jernkontorets Annaler.
Journal of the Agricultural Chemical Society of Japan.
Journal of Agricultural and Food Chemistry.
Journal of Agricultural Science.
Journal of the American Ceramic Society.
Journal of the American Chemical Society.
Journal of the American Leather Chemists' Association.
Journal of the American Oil Chemists' Society.
Journal of the American Pharmaceutical Association, Scientific Edition.
Journal of the American Society of Sugar Beet Technologists.
Journal of the American Water Works Association.
Journal of Applied Chemistry [London].
Journal of the Association of Official and Agricultural Chemists.
Journal of Biochemistry [Tokyo].
Journal of Biological Chemistry.
Journal of Chemical Education.
Journal of Chemical Physics.
Journal of the Chemical Society [London].
Journal of the Chemical Society of Japan, Industrial Chemistry Section.
Journal of the Chemical Society of Japan, Pure Chemistry Section.
Journal of the Chinese Chemical Society [Taiwan].
Journal of Clinical Endocrinology and Metabolism.
Journal of Clinical Pathology.
Journal of Colloid Science.
Journal of Comparative Pathology and Therapeutics.
Journal of Dairy Science.
Journal of the Electrochemical Society of Japan.
Journal of Electronics.
Journal of the Indian Chemical Society. Industrial Edition.
Journal of the Indian Institute of Science.

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JOURNALS

- Journal of Inorganic and Nuclear Chemistry.
 Journal of the Institute of Brewing.
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 Journal of Laboratory and Clinical Medicine.
 Journal of Marine Research.
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 Journal and Proceedings of the Oil Technologists' Association, India, Kanpur.
 Journal of Research of the National Bureau of Standards.
 Journal of the Rubber Research Institute of Malaya.
 Journal of the Science of Food and Agriculture.
 Journal of Scientific and Industrial Research [India]. Sections B and C.
 Journal of Scientific Instruments.
 Journal of the Society of Glass Technology.
 Journal of the Society of Leather Trades' Chemists.
 Journal of Soil Science.
 Journal of the South African Chemical Institute.
 Journal of the Taiwan Pharmaceutical Association.
 Journal of the Textile Institute, Transactions.
 Journal of Urology.
- Kautschuk und Gummi.
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 Kolloid-Zeitschrift.
 Kunststoffe.
- Laboratornoe Delo.
 Laboratory Practice.
 Lancet.
 Listy Cukrovarnické.
- Magyar Kémiai Folyóirat.
 Makromolekulare Chemie.
 Meddelelser fra Norsk Farmaceutisk Selskap.
 Mededelingen van de Vlaamse Chemische Vereniging.
 Medical Journal of Osaka University.
 Melland Textilberichte für die gesamte Technik der Textilindustrie.
 Mémorial des Poudres.
 Metal Finishing.
 Metall.
 Metallurgia [Manchester].
 Metallurgia Italiana.
 Mje Medical Journal.
 Mikrochimica Acta.
 Milchwissenschaft.
 Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene [Bern].
 Mitteilungen [Klosterneuburg]. Serie A, Rebe und Wein.
- Natural Science Report of the Ochanomizu University, Tokyo.
 Nature [London].
 Naturwissenschaften.
 New Zealand Journal of Science and Technology. B. General Research Section.
 Nucleonics.
- Ohio Journal of Science.
 Olii Minerali, Olii e Grassi, Colori e Vernici.
 Österreichische Chemiker-Zeitung.
- Paintindia.
 Paint Technology.
 Paliva.
 Papier [Darmstadt].
 Peintures-Pigments-Vernis.

JOURNALS

Perfumery and Essential Oil Record.
 Pharmaceutica Acta Helvetiae.
 Pharmaceutisch Weekblad voor Nederland.
 Pharmazeutische Zentralhalle für Deutschland.
 Pharmazie.
 Photoelectric Spectrometry Group Bulletin.
 Plating.
 Powder Metallurgy Bulletin.
 Praktische Chemie.
 Proceedings of the Indian Academy of Sciences.
 Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen. B and C.
 Proceedings of the Pennsylvania Academy of Science.
 Proceedings of the Society for Experimental Biology and Medicine.
 Proceedings. Soil Science Society of America.
 Przemysl Chemiczny.

Quarterly Reviews, Chemical Society [London].
 Química e Industria [Bilbao].

Radiation Research.
 Rapport du Commissariat à l'Energie Atomique, Centre d'Études Nucléaires de Saclay.
 Recueil des Travaux Chimiques des Pays-Bas.
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 Reports. British Coke Research Association.
 Reports of the Government Chemical Industrial Research Institute, Tokyo.
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Scandinavian Journal of Clinical and Laboratory Investigation.
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 Science [New York].
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Ukrainskii Khimicheskii Zhurnal.
United States Atomic Energy Commission. Reports.
United States Department of Interior, Bureau of Mines, Report of Investigations.

Verfkroniek.
Vestnik Moskovskogo Universiteta.
Vnitřní Lékařství.

Water and Sanitary Engineer.

Zavodskaya Laboratoriya.
Zeitschrift für analytische Chemie.
Zeitschrift für anorganische (und allgemeine) Chemie.
Zeitschrift für physikalische Chemie.
Zeitschrift für Elektrochemie.
Zeitschrift für Erzbergbau und Metallhüttenwesen.
Zeitschrift für Lebensmittel-Untersuchung und -Forschung.
Zeitschrift für Naturforschung.
Zeitschrift für Tierernährung und Futtermittelkunde.
Zeitschrift für Vitamin-, Hormon- und Fermentforschung.
Zentralblatt für Arbeitsmedizin Arbeitsschutz.
Zhurnal Analiticheskoi Khimii.
Zhurnal Neorganicheskoi Khimii.
Zhurnal Obshchei Khimii.
Zhurnal Prikladnoi Khimii.

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The organisations publishing the following journals are thanked for allowing reproduction of some abstracts.

British Baking Industries Research Association Abstracts.
British Cotton Industry Research Association. Summary of Current Literature.
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Rubber Abstracts.
Sugar Industry Abstracts.
Transactions of the British Ceramic Society.
Water Pollution Abstracts.

ERRATA

VOL. 3, 1956.

Abstract No.	Line
2738	26 for ferric read ferrous.
3160	3 for Eberlin read Eberlein.
3231	2 for G. Collier read G. L. Collier.
3330	8 for $\pm 2 \mu\text{g}$ read $\pm 0.2 \mu\text{g}$.
3745	13 for 50 ml read 5 ml, and for 20 ml read 20 μl .
3745	14 for 2 ml read 2 μl .
3745	21 for 500 mg read 500 μg .

VOL. 4, 1957.

Abstract No.	Line
342	2 for R. Ružička read E. Ružička.
380	1 for Diallylthiocarbamidohydrazine read Diallylthiocarbamidohydrazine.
412	3 for Pasgués read Pasqués.
459	1 insert of the acids after chemistry.
486	1 for Koste read Kosta.
658	2 for Okuma read Omura.
1015	3 for B. M. Wintermere read D. M. Wintermere.
1058	2 and 14 for Averill read Averell.
1120	4 for J. Vavrch read I. Vavrch.
1180	3 for Y. V. Morachevskii read Yu. V. Morachevskii.
1223	2 for L. N. Topalov read L. I. Topalov.
1273	19 for 1956 read 1955.
1351	4 for 1956 read 1955.
1416	7 for B.N.M.R.A. read B.N.F.M.R.A.
1511	3 for Shigol' read Shchigol'.
1545	3 for J. Kolařík read Z. Kolařík.
1679	3 for Ram Ji Das read Ramji Dass.
1765	4 for 1956, 1 (1) read 1956, 7 (1).
1972	3 for H. Hetzel read H. F. Hetzel.
2061	1 insert oxime after o-Hydroxyacetophenone.
2072	2 for Přibil read Přibil.
2122	8 for 1954 read 1955.
2330	8 for kynurenin read kynurenine.
2330	9 for hydroxykynurenin read hydroxykynurenine.
2345	2 for J. G. Llaurado read J. Garcia Llaurado.
2480	4 for Bruchenstein read Bruckenstein.
2579	1 for Photometric read Potentiometric.
2620	4 for Mappin read Mapper.
2957	3 for K. Shaver read K. J. Shaver.
3011	4 for Meloch read Meloche.
3035	2 for H. J. Waterman read H. I. Waterman.
3104	3 for Keiichiro read Kiichiro.
3159	4 for Hayashi read Hayami.
3240	7 for HNO_3 read nitrous fumes.
3240	10 for H_2SO_4 read sulphamic acid.
3270	2 for Shozo read Shouzow.
3270	3 for Misao read Misako.
3490	3 for N. Drake read N. A. Drake.
3535	4 for Shori read Shiro.
3552	4 for P. R. Kovalenko read P. N. Kovalenko.
3558	2 for Wentlandt read Wendlandt.
3588	2 for A. S. Meyer read A. S. Meyer, jun.
3587	3 for J. Přibil read R. Přibil.
3683	3 for F. Friedrich read K. Friedrich.
3773	2 for XL read XI .
3776	2 for M. N. Neustadt read M. H. Neustadt.
3908	2 for Seietzu read Seietsu.
3911	4 for L. Prat read L. Prat Perez.
3931	3 for Ankudinova read Ankudimova.

R.R.

ANALYTICAL ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1. The determination of the density of air and its influence on analytical weighing. A. von Lüpke (Sartorius-Werke A.-G., Göttingen, Germany). *Angew. Chem.*, 1956, **68** (16), 515-517.—The percentage variation in the density of air is given by $0.13 \Delta b - 0.35 \Delta t - 0.0005 \Delta f$, where Δb is the variation in atmospheric pressure (mm Hg), Δt is the variation in temp. ($^{\circ}$ C) and Δf is the variation in relative humidity (%). Nomograms are given for calculating variations in air density with change in b , t and f , corrections of weights for changes in buoyancy, and corrections of weights to vacuum.

A. R. ROGERS

2. The use of some organic substances as reducing reagents. V. Simon and J. Zýka (Inst. Anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (3), 571-575.—Some compounds used as developing agents in photographic developers have been tried as volumetric reagents (*Chem. Listy*, 1955, **49**, 1646). Only the *para*-substituted phenols (metol, *p*-aminophenol, *p*-phenylenediamine) react stoichiometrically, and the factor of a 0.1 N soln. remains constant for two months, although the solutions discolour. The end-point is best detected potentiometrically, but indicators may also be used. Iodine (down to 20 μ g) may be determined in Na_2CO_3 solution, Cl (down to 1 μ g) in HCl or H_2SO_4 solution, and BrO_3^- in 10 to 20% HCl or 10 to 50% H_2SO_4 by the potentiometric method; $\text{Cr}_2\text{O}_7^{2-}$, VO_3^- and Ce^{4+} can be titrated, with diphenylamine or ferroin as indicators. Two potential steps are found during the reduction of gold solutions, depending on the conditions, corresponding to the reduction to the univalent state and to the metal. Iron in moderate quantity does not interfere with any of these determinations, and if present in large excess may be complexed with F^- or PO_4^{3-} .

P. S. STROSS

3. Analytical use of some azo dyes of chromotropic acids: volumetric, gravimetric and spectrophotometric determinations. S. K. Datta (Chem. Lab., Darjeeling Gov. Coll., India). *Naturwissenschaften*, 1956, **43** (11), 250-251.—Dyes were prepared by diazotising ten different aromatic amino sulphonic and carboxylic acids and coupling them with chromotropic acid. The behaviour of these dyes towards Th, Zr, Fe and Ti was studied, and a list of their coloured complexes is presented. Some of the dyes are suitable for the spectrophotometric and volumetric determination of Th and Zr.

E. KAWERAU

4. Evaluation of 2-furoyltrifluoroacetone as an analytical reagent. R. T. McIntyre, E. W. Berg and D. N. Campbell (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1316-1318.—A 10% soln. of 2-furoyltrifluoroacetone in ethanol can be used for the detection of $\leq 2 \mu\text{g}$ of

some metal ions in 0.1 ml of soln. at pH 7 to 7.5. The reagent, which is non-specific, forms stable coloured or fluorescent metal complexes sol. in organic solvents. Heavy metals can thus be concentrated and separated by pptn. of the complexes, followed by extraction direct into an organic solvent or separation (*e.g.*, of Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+}) by ascending paper chromatography, with benzene-methanol (95:5) as solvent. Spectro- or fluoro-photometric determination of some metals with 2-furoyltrifluoroacetone is also possible, and the reagent can replace dimethylglyoxime as precipitant in the gravimetric determination of Pd in ores or alloys. W. J. BAKER

5. Alkaline solutions for pH control. R. G. Bates and V. E. Bower (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1322-1324.—A series of alkaline solutions useful for control of pH between 7 and 13 is prepared by adding standard solutions of HCl (0.1 M) or NaOH (0.1 or 0.2 M) to portions of the following stock solutions—tri(hydroxymethyl)methylamine (0.1 M), borax (0.025 M), sodium bicarbonate (0.05 M), disodium hydrogen phosphate (0.05 M) and KCl (0.2 M). The compositions and buffer values are tabulated (to intervals of 0.1 pH unit), and the dilution values and approximate temperature coefficient of pH are indicated. The estimated accuracy is within ± 0.02 pH unit; measured and calculated pH values agree well.

E. G. CUMMINS

6. "Phenylfluorone" as an acid-base indicator. M. N. Sastri (Chem. Lab., Andhra Univ., Waltair, India). *Naturwissenschaften*, 1956, **43** (8), 179.—"Phenylfluorone" is a suitable indicator for titrating strong acids with strong bases. The sample (50 mg) is dissolved in 5 ml of 0.1 N NaOH and made up to 100 ml with H_2O . The colour is rose in alkali and yellow in acid and a sharp end-point is observed in the titration. The indicator exhibits an orange-green fluorescence in daylight in a pH range of approx. 3 to 9.

E. KAWERAU

7. The leuco base of Bindscheller's green as redox indicator in chelatometry. P. Wehber (Lantziusstr. 13, Kiel, Germany). *Z. anal. Chem.*, 1956, **151** (4), 276.—The zinc-free leuco base, easily synthesised by reduction of the green dye in alkaline soln. with NaHSO_3 (*cf.* Wieland, *Ber. dtsh. chem. Ges.*, 1915, **48**, 1087), is as good a redox indicator as the more difficultly prepared Bindscheller's green. The zinc-free leuco base is ground with dried NaCl in the ratio 1:100, and 50 mg in aq. soln. is used for each titration. (*Cf. Anal. Abstr.*, 1956, **3**, 2088, 2504, 2712.)

P. S. STROSS

8. Volumetric analysis with Complexone III. O. Borchert (Härtol-Werk, Magdeburg, Germany). *Chem. Tech., Berlin*, 1956, **8** (6), 337-340.—A short review deals with the use of complexones for the

estimation of water hardness, Ca, Mg, Mg in the presence of Ca, Ba (Eriochrome black T or phthalein-complexone as indicator), Zn, Mn, Ni, Fe and Pb. P. S. STROSS

9. Thermometric titration curves. H. J. Keily and D. N. Hume (Mass. Inst. of Technol., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1294-1297.—Equations are derived for the relationship between temperature change and volume of titrant added in thermometric titrations. The effects of non-adiabatic conditions, the heat capacity of the apparatus, and change in volume during titration are derived and discussed. Heats of reaction, solution and dilution are estimated from automatically recorded thermometric titration curves by interpretation of slopes and the derived equations; results obtained are compared with literature values. E. G. CUMMINS

10. Quantitative spectrometric analysis in geology. Yu. A. Sherstkov. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1955, **19** (1), 117-119; *Ref. Zhur., Khim.*, 1956, Abstr. No. 7054.—In order to exclude the influence of the mineralogical composition of the samples, the determination of Fe, Ti, Ca and Mg in clays was carried out by dissolving the samples and introducing the soln. into the discharge by a special fulgurator. The ranges of concn. in percentages were Fe, 1 to 10; Ti, 0.6 to 2.5; Ca, 0.05 to 1.5; Mg, 0.05 to 1.2. The pairs of lines used were Fe 2599-39 - Co 2648-63; Ti 3349-04 - Co 3354-38; Ca 3938-47 - Co 3894-08; Mg 2802-7 - Co 2663-68 Å. R. LORD

11. Electrochemical methods of analysis. D. Bézier (L'Ecole Supérieure de Phys. et de Chim. de Paris, France). *Chim. Anal.*, 1956, **38** (8), 273-283.—A general review is made of the basic principles, applicability, advantages and limitations of the more important analytical procedures based on electrolysis, polarography, amperometry, potentiometry, coulometry and conductimetry. Emphasis is placed, with examples, on the value of polarisation curves for interpreting or predicting the electrochemical reactions, and for showing the interrelations of the various methods. W. J. BAKER

12. Catalysis and induction in redox reactions. VIII. Mutual and self-induction in electro-analytical precipitations. A. Schleicher (Frankenberger Str. 20, Aachen). *Z. anal. Chem.*, 1956, **151** (6), 413-415.—It is argued that the appearance of polarisation during electrolytic pptn. of metals such as Mn, Ni, Co and Fe, and during electrolytic liberation of H and O (which causes overpotential), may be regarded as self-induction due to the inhibition of primary mutual induction. J. P. STERN

13. Method for rapid analysis of very small gas samples. H. E. Lewis and O. G. J. Lippold (Dept. of Physiology, Univ. Coll., London). *J. Sci. Instrum.*, 1956, **33** (7), 254-256.—The gas sample (0.1 to 0.001 ml) is injected into water contained between two horizontal parallel plates. The area of the disc-shaped bubble is measured optically before and after the introduction of suitable absorbents. G. SKIRROW

14. Catalogue of infra-red spectra for qualitative analysis of gases. R. H. Pierson, A. N. Fletcher and E. St. Clair Gantz (U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1218-1239.—The catalogue gives the absorption spectra of 66 gases and vapours which

are likely to be present as products of combustion of rocket fuel. The spectra were obtained on a Perkin-Elmer model 21 i.r. spectrophotometer and cover the range of 2 to 15 μ . A chart of classified threshold values shows the sensitivity of the i.r. method for these gases and vapours under the conditions specified. P. T. BEALE

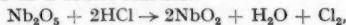
15. Manganese (II) carbonate and some of its valuable properties for gas analysis. E. Schulek and E. Pungor (Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1956, (7-8), 1116-1119.—*Preparation of reagent*—Dissolve $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (25 g) in H_2O (50 ml). Pour into a filtered soln. of NaHCO_3 (20 g) in H_2O (200 ml). Filter off the ppt. of $\text{MnCO}_3 \cdot 2\text{H}_2\text{O}$; wash it with H_2O and then with 98% alcohol ($\times 3$ or 4). Dry under air suction and remove the last traces of H_2O and alcohol with pentane. This prep. remains stable for 12 to 14 days. Water of crystallisation is lost at 70° to 100°, and at 250° to 300° pale-green MnO is formed. This is characterised by its ready absorption at 200°, not only of O, but also of gases that readily release O (NO , NO_2). At 450° to 500°, N_2O is absorbed. Thus the prep. may be utilised in gas analysis (*Anal. Abstr.*, 1957, **4**, 16) for the removal of traces of O from a number of gases, e.g., N and H. The surface area may be advantageously increased by mixing the $\text{MnCO}_3 \cdot 2\text{H}_2\text{O}$ with glass grit that has first been heated with HCl and then dried after washing with alcohol and pentane. D. F. PHILLIPS

16. New methods of gas analysis. II. Volumetric determination of gas mixtures. I. Iodimetric determination of oxygen. E. Schulek and E. Pungor (Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1956, (7-8), 1120-1135.—Methods are described for the determination of oxygen and nitrogen oxides in gas mixtures. For O, the principle is that of absorption by MnO (*cf. Anal. Abstr.*, 1957, **4**, 15) at 200° to 250° to form higher oxides of Mn which, after dissolution in HCl and addition of KI, are determined iodimetrically. The apparatus, which has been previously described (*cf. Mikrochim. Acta*, 1956, 1005), provides for the prep. of the MnO *in situ*. Macro- and micro-procedures are given for the determination of > 0.1% v/v and < 0.1% v/v, respectively. For nitrogen oxides, modifications of these methods are made whereby N_2O_3 or NO_2 is reduced to NO by means of KI, followed by thermal decomposition in the presence of MnO and subsequent iodimetric titration. The determination of N_2O necessitates prior decomposition of N_2O at 700° to 800°. In this case only about 90% recovery is obtained compared with 100% by the freezing-out method. D. F. PHILLIPS

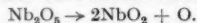
2.—INORGANIC ANALYSIS

17. Some applications of fusion reactions with zinc chloride in inorganic spot-test analysis. F. Feigl and A. Caldas (Min. Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1956, (7-8), 1310-1316 (in English).—Fusion with ZnCl_2 can readily accomplish reactions which are either impossible with conc. HCl soln. or which proceed but slowly. This is ascribed to the liberation of highly reactive anhyd. hydrogen chloride. Spot tests are described for the detection in silicates of 1 μg of Ca,

0.2 μg of Mg, 1 μg of K, 0.03 μg of Fe^{II} and Ni, following initial decomposition by fusion with ZnCl_2 (m.p. 365°). Fusion of Nb_2O_5 with ZnCl_2 results in a redox reaction—



but there is also an additional effect of heterogeneous catalysis in which a release of O is brought about by contact with molten ZnCl_2 —



As Ta_2O_5 remains unaffected by contact with molten ZnCl_2 , a differentiation of Nb_2O_5 and Ta_2O_5 is possible. *Procedure*—Free the test material from the oxides of Mo, W and V by digestion with aq. NH_3 and ammonium carbonate. Heat a little of the test material in a micro test-tube with several centigrams of ZnCl_2 over a free flame. If Nb_2O_5 is present a blue to blue-black ppt. is formed. The test will detect 10 μg of Nb in the presence of 100 μg of Ta. D. F. PHILLIPS

18. The reaction of acetylformazyl and of its derivatives with mineral ions. T. Dupuis (École Nat. Sup. de Chimie, 11 rue Pierre Curie, Paris, France). *Mikrochim. Acta*, 1956, (9), 1415-1421.—A study has been made of the possible use of acetylformazyl and its derivatives as reagents for spot-test analysis. Sensitive tests have been evolved by means of which Hg may be detected by using the thiosemicarbazone, and Cu and Pd may be detected by using the oxime. C. A. SLATER

19. Amperometric determination of heavy metals with mercaptobenzothiazole. J. Čihálik and E. Kudrnovská-Pavliková (Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, 21 (3), 718-724.—The amperometric determination of Pb, Cd and Cu with mercaptobenzothiazole (I) with a dropping-mercury electrode as cathode and a calomel electrode and potassium nitrate bridge as anode is described. A 30- μA meter and a 2-V accumulator are used to measure the current and apply the p.d. From 2 to 20 μg of Pb is determined in 20 ml by titration with I at pH 3 to 7 (acetate buffer) with an applied potential of 0.5 V; or 2 to 20 μg of Pb is pptd. and then just redissolved with KOH, 0.5 M KNO_3 is added and the soln. is titrated with I at an applied potential of 0.9 V. From 4 to 16 μg of Cd is determined in the presence of KNO_3 at pH 3 to 6 with an alcoholic soln. of I at an applied potential of 0.8 to 1.0 V. If Cu is present, the sum of Cu and Cd is obtained from a titration as above, and the Cu is determined by adding KCN soln. to a separate aliquot until the ppt. just redissolves and titrating immediately with an alcoholic soln. of I at an applied potential of 1.2 V. The difference of the two titrations gives the amount of Cd present. P. S. STROSS

20. Rapid determination of metals in organic products with alumina as spectrographic aid. P. L. Work and A. L. Julliard (Houdry Process Corp., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1261-1264.—From 0.001 to 7% of Ba, Ca, Zn, Fe, Ni or Pb can be determined spectrographically in 4 hr. (for one element) by mixing the sample with 7 to 50% of activated Al_2O_3 and using Cr or Co as internal standard. The additive acts as an excellent ashing catalyst, ash collector and spectrographic aid. The mixed sample and Al_2O_3 are heated at 600° for 2 hr. and the finely ground ashed product is mixed with the internal standard and compressed into pellets, six of which are arced between pure graphite rods (11.5 amp., 4-mm gap).

Line pairs and concn. ranges of the analytical curves are listed. W. J. BAKER

21. The influence of pH in the titration of metal ions with EDTA. Hisashi Nogami and Fujio Nakagawa (Pharm. Inst., Med. Fac., Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1955, 75 (10), 1287-1288.—The effect of pH on the compleximetric titration of various metals was examined and the minimum pH value for a satisfactory titration calculated. The value ranges from 8 (for Ba) to 0.8 (for Fe^{III}), decreasing with increase in formation const. of the metal-EDTA chelates. K. SAITO

22. High-frequency titration of some metal ions with EDTA. Hisashi Nogami and Fujio Nakagawa (Pharm. Inst., Med. Fac., Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1955, 75 (10), 1289-1290.—High-frequency titration curves of metal ions, including those of Cu, Ni, Zn, Fe, Pb, Cd and Ba, with EDTA were studied at various pH values. A clear point of inflection is obtained when metal ions forming stable complexes are titrated in an acid soln. The titration of Cu is applied to the determination of dimercaprol (BAL) in injections. The oily liquid (1 ml) containing 10% of dimercaprol and 20% of benzyl benzoate is dissolved in isobutyl alcohol (200 ml) and a 5-ml portion is mixed with 0.01 M $\text{Cu}(\text{NO}_3)_2$ (5 ml) and water (100 ml); the excess of Cu^{2+} is titrated with 0.005 M EDTA. K. SAITO

23. Quercetin as developing agent in the chromatography of inorganic compounds. J. Michal (Inst. Mining Res., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, 21 (3), 576-580.—Quercetin (I) is found to be a sensitive reagent for detecting Ag, Hg, Cu, Bi, Sb, Sn, Fe, Al, Ni, Co, Mg, Li, Mo, Be, Ga, In, Pr, Ne, Sm, U, V, W, Ti, La, Th, Zr and arsenate on paper. The sensitivity of I for each is given in a table. From absorption curves it is concluded that each atom of a bi-, ter- and quadrivalent metal combines with 2, 3 and 4 molecules of I, respectively. P. S. STROSS

24. Determination of micro quantities of hydrogen. Combustion - manometric method. B. D. Holt (Chem. Div., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1956, 28 (7), 1153-1157.—A combustion method that does not subject the sample to low pressure is described for the micro-determination of H in U, in ZrH_2 and in some organic compounds. The H is oxidised in a stream of oxygen and argon, and the H_2O produced is frozen out in a capillary U-tube trap that is cooled in acetone-dry ice. The U-tube swivels on semi-ball joints, and forms a constant-volume manometer. After the U-tube has been turned upwards, the H_2O is vaporised rapidly and its vapour pressure is measured. The method is sensitive to $< 0.1 \mu\text{g}$ of H. The subsequent determination of C is also possible by freezing out the CO_2 with liquid N. The simultaneous determination of H and C requires less than 30 min. J. H. WATON

25. Estimation of water by dielectric measurements. F. Oehme (Inst. für Mikrobiol. u. exp. Therapie, Jena, Germany). *Angew. Chem.*, 1956, 68 (14), 457-461.—A method for the determination of moisture content by the application of a high-frequency technique, which may be described as a dielectric analysis method, is given. It is necessary to measure the dielectric constant, dielectric loss,

and the conductivity of the material. The technique and method of calculating results are described. The water content of various crystalline compounds such as $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ may be estimated by this method. C. A. SLATER

26. Analytical applications of spectrophotometry of the system $\text{Cr}_2\text{O}_7^{2-} - 2\text{Cr}^{3+}$. IV. Quantitative determination of hydrogen peroxide. F. Capitán García and M. Lachica Garrido (Zaidan Exp. Sta., Granada, Spain). *An. Real Soc. Españ. Fis. Quim.*, B, 1956, **52** (4), 257-264.—A spectrophotometric method is proposed for the determination of H_2O_2 with $\text{K}_2\text{Cr}_2\text{O}_7$ as the reactive agent. A study is made of the factors that can affect the determination, such as the order of adding the reagents, the concn. of H_2SO_4 present, and the stability of the reagents. A max. error of $\approx 3\%$ is observed and the values of the average, standard, and probable deviations are given. Previous methods of estimating H_2O_2 are reviewed. Full experimental details and some typical results are given. (60 references.) C. A. FINCH

27. Electrochromatographic separation of alkali and alkaline-earth salts. H. Seiler, K. Artz and H. Erlenmeyer (Anstalt für anorg. Chem. der Univ. Basel, Switzerland). *Helv. Chim. Acta*, 1956, **39** (3), 783-786.—The method is described and R_F values are given for Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . The anions Cl^- , Br^- , I^- , SCN^- and PO_4^{3-} (R_F values given) can be identified at the same time. M. DAVIS

28. The role of flame temperature in the flame-photometric analysis of alkali metals. E. Pungor, A. J. Hegedüs, I. K. Thega and E. E. Zapp (Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1956, (7-8), 1247-1263.—A detailed investigation into flame processes is described. It is shown that temperature plays the dominant role and that measurement of flame temperature is advantageous in establishing optimum atomisation and combustion conditions. Stainless-steel atomising burners having easily interchangeable nickel capillaries are recommended and the atomisation should take place as close to the flame as possible. Prism or grating instruments are preferable to those in which filters are used. Lithium and Na are only slightly ionised in the oxy-hydrogen flame and in consequence there is no mutual interference in the determination of these elements, nor does their presence cause interference with the determination of K, Rb or Cs. On the other hand, K, Rb and Cs undergo considerable ionisation in the oxy-hydrogen flame, resulting in increased emission of these elements and hence considerable interference with one another. This can be largely overcome by mixing about 50% of N with oxy-hydrogen which reduces the flame temperature by $> 1000^\circ$ without disturbing the other parameters. The loss of sensitivity thereby experienced is not considered to be serious in view of the generally high sensitivity of flame-photometer methods. D. F. PHILLIPS

29. Interference of barium in the flame-photometric determination of sodium, potassium and calcium. J. Ramírez-Muñoz and F. Burriel-Martí (Madrid Univ., Spain). *An. Real Soc. Españ. Fis. Quim.*, B, 1956, **52**, 169-176.—The effect of Ba on the determination of Na, K and Ca by flame photometry has been studied, with particular reference to the determination of the three elements in soil extracts obtained by extraction with Ba acetate.

The effect of the addition of Ba acetate to test soln. and to standard soln. for reducing the deviations resulting from the presence of different amounts of Ba, and the optimum concn. of the three elements for measurement have been examined. L. A. O'NEILL

30. Continuous measurement of the concentration of sodium chloride solution by means of a high-frequency apparatus. Sôichirô Musha, Takeo Yano, Masami Takeda and Takeshi Wada (Dept. of Applied Chem., Fac. of Eng., Osaka Prefectural Univ., Sakai, Osaka). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (7), 482-485.—A beat-type high-frequency meter was devised for the continuous measurement of the concn. of aq. NaCl soln. ($< 20\%$). The sample soln. is passed through a glass container (diameter 7.5 mm) placed between two brass plates connected to an oscillator (7.4 Mc per sec., fluctuation ± 1 to 25 Kc). The high-frequency wave is mixed with a standard wave of 7.4 Mc coming from a quartz oscillator, and the beat is amplified and rectified to be measured with a d.c. milli-ammeter. To protect the container from change in humidity and temp., it is covered with a sheet of poly(vinyl alcohol) and silica gel is placed in it. Fluctuation resulting from variable rate of flow is of negligible order. The deviation from the chemically determined value is $< 6\%$. K. SAITO

31. Continuous measurement of the concentration of sodium sulphate and ammonium sulphate solution by means of a high-frequency apparatus. Sôichirô Musha, Masami Takeda, Takeshi Wada and Etsuo Inoue (Dept. of Appl. Chem., Fac. of Eng., Osaka Prefectural Univ., Sakai, Osaka). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (7), 486-490.—The beat-type high-frequency meter (*Anal. Abstr.*, 1957, **4**, 30) was modified for use in the continuous measurement of concn. of Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ soln. The sample container (condenser cell) was covered with a metal tube to keep the temp. const. and a thermistor was attached for automatic control of the temp. A monitor circuit was also attached to check the constancy of the oscillation. The new apparatus enables an accurate measurement (relative error $\approx 2.5\%$) of the concn. of Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ ($\approx 20\%$) to be made. K. SAITO

32. Separation and purification of milligram amounts of caesium from large amounts of other alkali salts. S. A. Ring (Nat. Carbon Res. Lab., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1200-1201.—Milligram quantities of Cs can be separated from a small excess of Rb and a large excess of Na on a phenolic methylenesulphonic resin such as Duolite C-3. The soln. of the alkali metals is applied in 0.5 N NaOH soln., and the resin is eluted with 0.5 N NaOH. The Cs is finally stripped with 6 N HCl, and has a Rb content of < 2 parts per thousand. Final removal of Cs from Na and K requires one or more pptn. J. H. WATON

33. The separation of fission products. Preparation of carrier-free radioactive caesium. Takanobu Shiokawa and Masuo Yagi (Sch. of Chem., Fac. of Educ., Shizuoka Univ., Oiwa-cho, Shizuoka). *Japan Analyst*, 1956, **5** (4), 220-221.—The separation of radioactive Cs from other fission products was studied with tungstophosphoric acid in place of tungstosilicic acid (Turkevich *et al.*, *Phys. Rev.*, 1951, **84**, 52). The separation proceeds satisfactorily, Cs being co-pptd. with NH_4^+ with chloroplatinic acid from a neutral soln. of caesium

tungstophosphate. By thermal decomposition of the $(\text{NH}_4)_2\text{PtCl}_6$ at 600° and filtration of Pt, carrier-free Cs is obtained as chloride. No significant contamination by ^{90}Sr , ^{90}Zr , ^{106}Ru , ^{144}Ce , ^{124}Sb or their decay products was observed. K. SAITO

34. Volumetric determination of copper in bearing metal. C. Freitag (Metal Testing Office 321, Karl-Marx Stadt). *Chem. Tech., Berlin*, 1956, **8** (2), 81-82.—A rapid method (15 min.) is described for estimating the Cu in bearing metals in the presence of Sn, Sb, Pb and other foreign components. It is based on the known process of reducing cupric salts in acid soln. by KI, with the liberation of the equiv. amount of I (which is titrated with $\text{Na}_2\text{S}_2\text{O}_3$), but the method is improved by effecting the reduction in the presence of KSCN (or NH_4SCN) to give an immediate separation of the Cu^+ as difficultly sol. CuSCN and hence to ensure that the reduction reaction with KI proceeds quant. to completion without the use of a large excess of KI. The metal borings (1 g) in a 300-ml Erlenmeyer flask are treated successively with 10 ml of water, 10 ml of 40% HF, and 10 ml of HNO_3 (sp. gr. 1.4). On completion of the vigorous dissolving reaction, 5 ml of H_3PO_4 (sp. gr. 1.7) is added and the soln., after being boiled for a short time, is diluted with 100 ml of water. Solid urea is then added until no evolution of gas results (showing destruction of any nitrite). After cooling, the soln. is treated with 10 ml of a urea-Pb(NO_3)₂ soln. [100 g of urea and 1.5 g of Pb(NO_3)₂ per litre]. Then 10 ml of thiocyanate-I soln. (containing 100 g of KSCN or NH_4SCN per litre) is added and the soln. is immediately titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, the main part of the liberated I being titrated first and then, after adding 2 ml of starch soln., titration is continued to the pale-brown end-point. The Cu equiv. of the 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ soln. is obtained by determination against pure Cu or metal of known Cu content.

H. L. WHITEHEAD

35. Simultaneous micro-determination of copper and iron using mixed phenanthrolines. B. Zak and N. Ressler (Wayne Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1158-1161.—Photometric methods are investigated for the simultaneous determination of Cu and Fe up to a concn. of 5 p.p.m., such as might be encountered in normal and pathological serum. Adequate results are given by two methods based on the measurement of the extinction of a soln. of the metal complexes at two wavelengths, followed by mathematical analysis. In these methods use is made of aq. soln. of Fe^{II} -1:10-phenanthroline (I) and Cu^{II} -2:9-dimethyl-1:10-phenanthroline (neocuproine) (II) complexes, with the extinctions measured at 454 and 510 μ , and of isoamyl alcoholic soln. of Fe^{II} -4:7-diphenyl-1:10-phenanthroline (bathophenanthroline) and II complexes, with the extinctions measured at 454 and 535 μ . Somewhat better results are obtained if, after preparing an aq. soln. of I and II, II is extracted in isoamyl alcohol, and the extinctions of the aq. and alcoholic soln. are measured at 510 and 454 μ , respectively.

J. H. WATON

36. Controlled potential electrolysis. I. Counter microcoulometer and its application to the coulometric determination of copper, lead and cadmium. Masaichiro Masui and Hiriteru Sayo (Pharm. Fac., Osaka Univ., Hotarugaikae, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1956, **75** (12), 1515-1519.—A simple microcoulometer was constructed by modifying Kramer's circuit (*Anal. Chem.*, 1954, **26**,

415) so as to use a blocking oscillator. The resistance of the grid circuit of the 6SJ7-GT tube automatically changes with change in the electrolytic circuit, so that the frequency of the oscillator remains constant throughout the electrolysis. This was used for the determination of Cu (12 to 200 μ g), Pb and Cd (\approx 100 μ g) (cathode potential, -0.24, -0.5 and -0.70 V, respectively) in an acid soln. containing tartrate (for Cu) or in 0.1 M KCl soln. (for Pb and Cd). The overall error is \approx 1 μ g for each ion; the error is greater for Cd and Pb in their mixtures.

K. SAITO

37. Analysis of beryllium. XVII. Separation of beryllium from other metals with oxine. Tomoyuki Akiyama (Kyoto Coll. Pharm., Higashiyama-ku, Kyoto). *Japan Analyst*, 1956, **5** (4), 212-216.—The methods of Knowles (*J. Res. Nat. Bur. Stand.*, 1935, **15**, 87) and Fischer (*Wiss. Veröff. Siemens*, 1933, **12**, 44) for the separation of Be from other metals, including Fe, Cu, Zn, Ni and Ti, were re-examined for use in the determination of Be in beryl and related minerals. The average deviation is \approx 0.1% (absolute).

K. SAITO

38. Solubility product of beryllium hydroxide. I. M. Korenman, F. S. Frum and G. A. Tsygankova (Gorki State Univ.). *Zhur. Obshch. Khim.*, 1956, **26** (6), 1558-1560.—The solubility product of $\text{Be}(\text{OH})_2$, determined by the method of Akselrud and Fialkov (*Ukrain. Khim. Zhur.*, 1950, **16**, 294), is 3.5×10^{-18} from measurements in 0.03 to 0.2 M soln. and 2×10^{-18} from measurements in 0.001 to 0.002 M soln. The solubility, determined directly, of $\text{Be}(\text{OH})_2$ in water at room temp. is 2.2×10^{-4} M. The first dissociation const., calculated from the solubility product and the solubility and the known value (5×10^{-11}) of the second dissociation const. is 1.8×10^{-4} . G. S. SMITH

39. Rapid determination of magnesium in basic slag by the use of ethylenediaminetetra-acetic acid. Shigeo Wakamatsu (Toto Seiko Co., 5, Minami-suna-machi, Koto-ku, Tokyo). *Japan Analyst*, 1956, **5** (5), 264-267.—A rapid (\approx 10 min.) determination of Mg in basic slag was studied with reference to the elimination of interference by other metal ions. The effect of Mn and Al is eliminated by the addition of Fe (the sum of FeO and Fe_2O_3 should be $>$ 7 times the weight of the Al_2O_3 and $>$ 2 times that of the MnO). No significant interference results from other ingredients, including Ca, P and F. *Procedure*—The sample (0.1 g) is dissolved in HNO_3 (1 + 1, 10 ml), diluted with water (120 ml), ammonium acetate soln. (50%, 20 ml) and ammonium oxalate (saturated soln., 30 ml), boiled for 2 min. and filtered. A portion of the filtrate is mixed with water (50 ml) and KCN soln. (5%, 10 ml) (masking agent for Fe) and adjusted to pH 10 with aq. NH_3 soln. This is titrated with 0.01 M EDTA (disodium salt) (indicator Eriochrome black T); Ca is determined in the residue.

K. SAITO

40. Determination of free lime and carbonate in calcium silicate hydrates by thermobalance. F. M. Biffen (Johns-Manville Res. Centre, Manville, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1133-1136.—A thermogravimetric method for the determination of free lime and carbonate gives results more accurate than those obtainable by the usual extraction and gravimetric methods, respectively. The method is particularly more reliable when the amounts to be determined are small. In the absence of appreciable

amounts of carbonaceous matter, one thermolysis curve suffices for the determination of water, free lime and carbonate.

J. H. WATON

41. Volumetric determinations of barium and sulphate ions. I. Determination of barium by iodimetry. F. de A. Bosch Ariño and M. Peris Gomez (Valencia University, Spain). *An. Real Soc. Españ. Fis. Quim.*, B, 1956, **52**, 187-198.—The optimum conditions for the pptn. of Ba^{2+} as $BaSO_4 \cdot H_2O$ have been studied and the following procedure for the determination of Ba developed. The soln. of barium salt is treated with an excess of aq. $Na_2S_2O_3$ (3.5 ml of 0.1 N $Na_2S_2O_3$ per 1 ml of Ba^{2+} , 0.1 M) and ethanol (96%) equivalent in wt. to the H_2O present, at 20° to 30° and pH 4.5 to 7. After alternate periods of shaking and settling, the ppt. is filtered off and the excess of $Na_2S_2O_3$ determined iodimetrically; Sr^{2+} at concn. of 0.003 M are pptd. with the Ba^{2+} ; Ag^+ , Pb^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} , Ni^{2+} and Co^{2+} interfere, but not Ca^{2+} , Mg^{2+} , Mn^{2+} , Cd^{2+} or Zn^{2+} .

II. Indirect volumetric determination of sulphate. F. de A. Bosch Ariño and M. Peris Gomez. *Ibid.*, 1956, **52**, 199-206.—The SO_4^{2-} are pptd. with an excess of 0.1 M $BaCl_2$ and the excess of Ba^{2+} is determined volumetrically as in Part I. There is interference from $HClO_4$ (sometimes used to solubilise org. compounds of S) at concn. > 0.4 mg per 5 ml, also from various anions that give an insol. ppt. with Ba^{2+} , but not from NO_3^- . The method has been successfully used on drinking water, cements and sol. org. sulphates.

L. A. O'NEILL

42. X-ray fluorescence determination of barium, titanium and zinc in sediments. G. J. Lewis, jun., and E. D. Goldberg (Scripps Instn. Oceanography, La Jolla, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1282-1285.—Quant. procedures are given for the rapid determination, by X-ray fluorescence spectroscopy, of Ba, Ti and Zn in calcareous muds, glauconitic and deep-sea clays, etc. Matrix effects in the samples (1 g of 300-mesh material) are minimised by internal standards, viz. As_2O_3 for Zn, and La_2O_3 for Ba and Ti. Corrections are made for the overlapping effect of the $Ba L\alpha_1$ and $Ti K\alpha$ peaks, which have the max. usable sensitivities. For Ti or Ba contents of 0.1 to 2.0%, the absolute counting error varies from 4 to 10%, and for Zn contents of 0.004 to 0.6% it varies from 4 to 15%. The results agree with those obtained by emission spectrography.

W. J. BAKER

43. The spectrophotometric determination of the alkaline-earth metals with murexide, Eriochrome black T and with o-cresolphthalein complexone. F. H. Pollard and J. V. Martin (Univ., Bristol, England). *Analyst*, 1956, **81**, 348-353.—In the absorptiometric method with murexide the procedure of Williams *et al.* (*Anal. Abstr.*, 1954, **1**, 249) is modified. The soln. containing Ca and a blank soln. are treated at pH 11.3 with a murexide soln. by a procedure that ensures that reaction between the murexide and each soln. occurs simultaneously and to the same extent. The extinction of each soln. is measured at 506 m μ . The calibration graph is linear up to 1.2 mg of Ca per litre. Strontium, up to 10 mg per litre, is determined by a similar procedure, the extinction being measured at 515 m μ . Magnesium is determined by a modification of the method of Harvey *et al.* (*Anal. Chem.*, 1953, **25**, 498). The soln. is adjusted to pH 10-15 and a methanolic soln. of Eriochrome black T is

added, the technique being similar to that used for Ca. The extinction is measured at 520 m μ . The procedure for the determination of Ca with o-cresolphthalein complexone soln. (prep. described) at pH 10-15 is similar, the extinction being measured at 575 m μ . The calibration graph is slightly curved. Strontium is determined similarly at pH 10-6 and 575 m μ and the use of this complexone is very satisfactory for the determination of Ba at pH 11-3 and 575 m μ .

A. O. JONES

44. The quantitative analysis of the alkaline-earth metals by paper chromatography. F. H. Pollard, J. F. W. McOmie and J. V. Martin (Univ., Bristol, England). *Analyst*, 1956, **81**, 353-358.—A paper-chromatographic method is described for the quantitative determination of microgram amounts of mixtures of Ba, Sr, Ca and Mg. The metals are separated as formates by downward elution on Whatman No. 1 paper in the apparatus of Elbein *et al.* (*Brit. Abstr. C*, 1950, 428). The eluting solvent consists of methanol (50 ml), isopropyl alcohol (30 ml), formic acid (2 ml), water (15 ml) and ammonium formate (2.5 g). On untreated paper, Ba and Sr are detected by spraying with sodium rhodizonate, Ca with pyrogallol-4-carboxylic acid and Mg (and Be) with 8-hydroxyquinoline. On acid-washed paper, 8-hydroxyquinoline is very sensitive to all the metals that emit a green fluorescence with NH_3 vapour under u.v. light. On untreated paper, this is masked by the strong background fluorescence of calcium and magnesium impurities. The rhodizonate test is preferable for Ba. The positions of the separated metals are ascertained by comparison with a pilot chromatogram to which the identifying reagents are applied. Methods are described for the extraction of the metals from the chromatogram. They are then determined spectrophotometrically (*cf.* *Anal. Abstr.*, 1957, **4**, 43).

A. O. JONES

45. The influence of tartrates and citrates on the determination of zinc by various methods. F. S. Shpilev. *Trudy Dagest. Sovetskikh. Inst.*, 1955, **7**, 119-129; *Ref. Zhur., Khim.*, 1955, Abstr. No. 52,145.—The presence in the soln. of ammonium tartrate in concn. < N does not cause interference in the quant. determination of Zn^{2+} by the phosphate method. With a concn. of ammonium citrate > 0.5 N, Zn^{2+} are not pptd. as $ZnNH_4PO_4$. The accuracy of the determination of Zn by the phosphate method in the presence of ammonium citrate depends on many factors [pH, quantity of citrate, $(NH_4)_2HPO_4$, NH_4Cl , etc.]. The same effects are also observed in the determination of Zn by the carbonate method in the presence of alkali-metal salts. The more $(NH_4)_2HPO_4$ is added to the soln. of zinc salts and ammonium citrate, the higher are the results obtained for Zn, although the Zn^{2+} are not quant. pptd. The higher the concn. of Na tartrate or citrate in the soln., the greater is the error in the determination of Zn^{2+} by carbonate. In all cases colloidal ppt. and soln. are observed. A complete separation of Zn^{2+} as sulphide is effected in the presence of ammonium tartrate or citrate, and this method gives satisfactory results.

C. D. KOPKIN

46. Amperometric determination of cadmium by ferrocyanide. N. A. Ramaiah, S. K. D. Agarwal and S. L. Gupta (Dept. Phys. Chem., Indian Inst. Sugar Technol., Kanpur, India). *Naturwissenschaften*, 1956, **43** (9), 197.—The titration is carried

out at neutral pH with a manually operated dropping-mercury electrode, 1.0 M KCl being used as the supporting electrolyte. The titration curves are L-shaped and a clear end-point is obtained when a known quantity of Cd^{2+} reacts with an equimolar amount of ferrocyanide. From the titrations it is deduced that the composition of the ppt. is $\text{CdK}_2[\text{Fe}(\text{CN})_6]$ over the entire range.

E. KAWERAU

47. Titration of mercury with bis(2-hydroxyethyl)-dithiocarbamate. J. S. Fritz and S. A. Sutton (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1300-1303.—Macro amounts of Hg^{2+} , in acetone- H_2O (3:7 by vol.) as solvent, can be determined accurately in the presence of Cl^- , Br^- and metal ions by direct titration with 0.02 N di(2-hydroxyethyl)dithiocarbamate (**I**) in the presence of EDTA (disodium salt) and $\text{Cu}(\text{NO}_3)_2$ at a pH of ≈ 7 . After formation of the colourless complex of **I** with Hg^{2+} is complete, the first slight excess of **I** reacts with Cu^{2+} to form an intense yellow complex. The concn. of Cu^{2+} in the soln. should be $\geq 10^{-3}$ M. The titration can also be made (i) with a 0.1% soln. of 4:4'-di(dimethylamino)thiobenzophenone (a thio derivative of Michler's ketone) in acetone as visual indicator, or (ii) potentiometrically with a silver-silver dithiocarbamate indicator electrode, the visual end-point appearing approx. at the steepest part of the potentiometric curve. Interference is caused by Ag^+ , Au^+ , CN^- , SCN^- , citrate and arsenite; Bi and Cr^{3+} cause high results, whilst Fe^{3+} cause slightly low results. Large amounts of metal ions should be removed initially by passing the sample soln., containing an excess of Cl^- , through a cation-exchange column.

W. J. BAKER

48. Improved spot test for boron and a quantitative estimation of boron in very dilute solutions. T. S. Burkhalter and D. W. Peacock (Agric. and Mech. Coll. of Texas, College Station, U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1186-1188.—A spot-test procedure based on the change in pH due to the formation of the boric acid-polyhydric alcohol complex with sorbitol will detect 0.003 μg of B. If the sensitivity is varied by using other polyhydric alcohols, a rough quant. method for small amounts of B is established.

J. H. WATON

49. The quantitative micro-determination of boron by measurement of the pH of mannitoboric acid. F. Csapó, M. Bihari, M. Gilde and E. Sztankó (Távközlési Kutató Int., Budapest, Hungary). *Z. anal. Chem.*, 1956, **151** (4), 273-276.—By measurement of the pH change following the addition of mannitol to the test soln., as little as 0.01 μg of boron may be estimated. In the presence of interfering substances, e.g., metal salts and silicon, the estimation is preceded by a distillation of the boron as methyl borate, which is subsequently saponified. Free 50 ml of the sample soln. from CO_2 by bubbling N through it, adjust to pH 6.0, add 3 g of mannitol and measure the pH. The amount of borate is determined from a calibration curve or from the known dissociation constant of mannitoboric acid.

P. S. STROSS

50. The isotopic analysis of boron by mass spectrometry. G. H. Palmer, D. F. Dance and K. L. Aitken (A.E.R.E., Harwell, England). A.E.R.E. Report, GP/R 1994, 1956, 8 pp.—The isotopic analysis of boron, in which BF_3 ionised by electron bombardment (90 eV) and sodium borate ionised by a hot tungsten filament (900°) are used, is dis-

cussed. The ^{11}B to ^{10}B ratio of the boron sample is determined from measurement of the relative intensities expressed in the mass 49:mass 48 ratio and the 89:88 ratio, respectively. The significance of addition peaks is considered. The "memory effect" experienced in routine operations, most important when the relative concn. of the two isotopes differ considerably from that of natural material, has been investigated. The lengthy procedure necessary with the most efficient of the three manifolds, designed to minimise the effect, is detailed.

E. G. CUMMINS

51. Analytical applications of spectrophotometry of the system $\text{Cr}_2\text{O}_7^{2-}$ - 2Cr^{3+} . V. Quantitative determination of perborates. F. Capitán García and M. Lachica Garrido (Zaidan Exp. Sta., Granada, Spain). *An. Real Soc. Españ. Fis. Quím., B*, 1956, **52** (4), 265-270.—A spectrophotometric method for the determination of perborates is proposed, in which $\text{K}_2\text{Cr}_2\text{O}_7$ is used as the reagent. A study is made of the influence of the order of adding the reagents, the concn. of acid, and the stability of the solutions. The max. error of the method is $\approx \pm 5\%$; estimates of the average, standard, and probable deviations are made. Full experimental details and a number of typical results are given. Previous methods for the estimation of perborates are reviewed briefly. (14 references.)

C. A. FINCH

52. Simple indicator method for determination of aluminium. R. V. Paulson and J. F. Murphy (Kaiser Aluminum and Chem. Corp., Spokane, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1182-1184.—The alkalimetric method for the determination of Al described by Bushey (*Anal. Chem.*, 1948, **20**, 169), and which is applicable in the presence of F^- , is modified by carrying out the pptn. of cryolite in alkaline soln. and by using an indicator instead of pH measurements. After the pptn. of cryolite at pH 9-8, the OH^- -liberated are titrated with standard acid to pH 9-35. The indicator used is a mixture of thymolphthalein and alizarin yellow. As the liberation of OH^- is not stoichiometric, the acid must be standardised against known soln. of Al. For amounts of Al of ≈ 4.5 mg, the method is as reliable as the original, but it becomes less accurate for larger amounts of Al. Interference from NH_4^+ , Fe^{3+} and Cr^{3+} is eliminated by boiling and filtering before the titration, and CO_3^{2-} are removed by the addition of BaCl_2 .

J. H. WATON

53. Ion exchange - spectrophotometric determination of aluminium. A. D. Horton and P. F. Thomason (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1326-1328.—In the determination of Al in Cu-Al, U-Al and Sn-Pb alloys, stainless steel, and iron alloys, the many separations of interfering metals usually necessary in the aluminon method can be avoided by separating Al from these other metals with Dowex-1 anion-exchange resin (Cl form) from a 9 M HCl soln. of the sample. The Al in the eluate is determined as the ammonium aurintricarboxylate lake at 525 μm in a 1-cm cell. If the sample contains Pb, this can be separated by adjusting the eluate (9 M HCl) to 2 M HCl and passing it through a second ion-exchange column. Interference by Ni^{2+} can be masked by adding conc. HCl and 12 M aq. pyridine to the eluate; if Cr is present in an amount greater than that of the Al, the sample should be treated with HClO_4 and HCl. Small amounts of Ti^{3+} and Mn^{2+} do not seriously interfere. The accuracy is

within $\pm 0.10\%$. The final soln. (50 ml) should contain from 5 to 50 μg of Al. W. J. BAKER

54. Liquid-liquid extraction procedures in inorganic analysis. III. T. S. West (Dept. of Chem., Univ. of Birmingham, England). *Metallurgia, Manchr.*, 1956, **53**, 185-188.—Procedures for group 3 metals are described. The extraction of Al as its chelate with oxine by CHCl_3 is complete between pH 4.3 and 4.6. Small amounts of Al are completely extracted at pH 2.5 by cupferron and CHCl_3 ; GaCl_3 is readily extracted from aq. soln. by diethyl ether at acidity 6 N (distribution coeff. ≈ 17). The chelate of 8-hydroxyquinoline with Ga can be extracted from aq. solution at pH 2.6 to 3.0 by CHCl_3 and thus separated from Al (but not In). Methods of separation of In, Tl and the rare earths are also reviewed. S.C.I. ABSTR.

55. Carbonate method of determining the acidity of aluminosilicates. K. G. Miessarov (Inst. of Petroleum, Acad. Sci., USSR). *Zhur. Prikl. Khim.*, 1956, **29** (6), 851-855.—The sample (2-5 g) of aluminosilicate is mixed with 100 ml of a suspension of BaCO_3 in N NaCl and periodically shaken during 24 hr. The BaCO_3 is then removed by shaking with N NaCl and decantation of the soln. The treated sample is twice washed with CO_2 -free water and after being dried at 100° is treated with small amounts of a standard solution of HCl. The soln. are decanted into a 250-ml calibrated flask and the amount of acid used in removing the Na absorbed by the aluminosilicate is determined by titration with 0.03 N NaOH to the phenolphthalein endpoint. With bentonite, absorption of acid also occurs. Allowance for this is made by finding the acid absorption of the original material. Since BaCO_3 is absorbed by some aluminosilicates in the first operation and any remaining would give faulty results, it is necessary to ensure that all the BaCO_3 used is removed. G. S. SMITH

56. Fluorimetric micro-determination of gallium with dibromoxine [5:7-dibromo-8-hydroxyquinoline]. I.-M. Ladenbauer and O. Slama (Chem. Univ. Lab., Vienna, Austria). *Mikrochim. Acta*, 1956, (7-8), 1219-1224.—Following a preliminary separation of Ga (in dil. HCl soln.) from most other ions which cause fluorescence-quenching, by means of ether extraction, Ga is extracted with 5:7-dibromo-8-hydroxyquinoline (I) reagent and CHCl_3 from the dil. acid soln. after removal of ether. The fluorescence of the Ga dibromo-oxinate is measured in a photo-electric fluorimeter under u.v. irradiation. The concn. range studied was from 0.25 to 1 μg of Ga per 6 ml of CHCl_3 . *Procedure*—To the gallium chloride soln. in a porcelain dish add 10% NaCl soln. (0.5 ml) and evaporate to dryness. Dissolve the residue in 0.1 N HCl (2 ml). Add further 0.1 N HCl (2 ml) and transfer to a glass-stoppered flask. Add H_2O (1 ml) and 20% hydroxylamine hydrochloride soln. (1 ml) and 0.2 M K H phthalate soln. (6 ml). Add 0.1 ml of I reagent (0.25 g of I dissolved in 20 ml of conc. HCl, and made up to 100 ml) and shake with double-distilled CHCl_3 (6 ml). Immediately measure the fluorescence in the CHCl_3 layer in a fluorimeter.

D. F. PHILLIPS

57. Separation of gallium from trivalent iron by means of ion exchange. J. Korkisch and F. Hecht (Chem. Univ. Lab., Vienna, Austria). *Mikrochim. Acta*, 1956, (7-8), 1230-1237.—Both Ga and Fe in weak HCl soln. of KSCN form negatively charged

thiocyanate complexes which are retained by the strongly basic ion-exchange resin Amberlite IRA-400. The chromatographic separation of the two elements is based on the different stabilities and migration velocities of these complexes when they are eluted from the resin column with 0.1 N HCl, the Ga preceding the Fe. If Al ($> 2 \text{ mg}$) is present (e.g., in bauxite) it can be removed from the column by washing with a weak acid soln. of KSCN. Separation of 15 μg of Ga from a max. of 1.25 mg of Fe can be accomplished with recoveries of 96 to 98% of Ga. If the content of Fe is $> 0.5 \text{ mg}$, up to 100 μg of Ga can be separated. Fluorimetry is used to determine the eluted Ga, with Solochrome red ERS or Solochrome black W DFA (cf. *Anal. Abstr.*, 1956, **3**, 1654). The presence of KSCN in the eluate does not cause interference with the fluorimetry. D. F. PHILLIPS

58. Paper-chromatographic separation of gallium from iron, titanium and aluminium and its fluorimetric determination with 5:7-dibromo-8-hydroxyquinoline. O. Slama and I.-M. Ladenbauer (Univ. Vienna, Austria). *Mikrochim. Acta*, 1956, (7-8), 1238-1246.—For the complete separation of Ga from several times as much Fe, Al and Ti, the paper-strip apparatus previously described (cf. *Anal. Abstr.*, 1955, **2**, 3006) for the separation of Ge was used. The sample was treated for 40 hr. with a solvent of *n*-butanol-glacial acetic acid-ethyl acetoacetate- H_2O (50:10:5:35, by vol.). Difficulties were experienced in determining the separated Ga with 5:7-dibromo-8-hydroxyquinoline (I) (*Anal. Abstr.*, 1957, **4**, 56) or by the use of Solochrome red ERS and Solochrome black W DFA (*Anal. Abstr.*, 1956, **3**, 1654) owing to interference from Fe and Cu present in the chromatography paper. The fluorimetric method with I was successfully modified to overcome these difficulties. *Procedure*—Pass 80 ml of 6 N HCl soln. containing several micrograms of Ga and about 1000 times as much Fe and Ti through a silver reductor; mix the product with a saturated soln. of TiCl_3 (4 ml) and extract in the Hahofer and Hecht ether extractor (illustrated) for 4 hr. with 50 ml of ether. In the ether-holding flask is 10 ml of H_2O . After completion of the extraction, evaporate the ether under reduced pressure and evaporate the aq. soln. to dryness in a platinum crucible. Dissolve the residue in 0.1 N HCl (0.2 to 0.3 ml) and add the soln. dropwise to the chromatographic paper strip. After 40 hr. develop the chromatogram with alizarin. Cut the strip and elute Ga as previously described for Ge (*Anal. Abstr.*, 1955, **2**, 3006) with 0.1 N HCl. Evaporate the eluate to dryness in a platinum crucible, dissolve the residue in 0.1 N HCl (0.2 ml) and finish fluorimetrically with I as previously described (cf. *Anal. Abstr.*, 1957, **4**, 56). Recoveries were about 95% on 1 to 2 μg of Ga taken. Results are quoted for determinations of Ga made on samples of petroleum-bore waters by using the methods described, which are both accurate and rapid. D. F. PHILLIPS

59. Electrolytic separation and volumetric, absorptiometric and coulometric estimation of thallium. W. T. Foley and R. F. Pottie (St. Francis Xavier Univ., Antigonish, Nova Scotia, Canada). *Anal. Chem.*, 1956, **28** (7), 1101-1104.—Univalent thallium can be separated quant. by controlled potential electrolysis from ammoniacal NH_4NO_3 soln., with Ag^+ as depolariser. The Tl is deposited on the anode as an oxide, which is probably hydrated Tl_2O_3 , of equiv. wt. 116.4. In

the absence of interfering ions, the wt. of Ag deposited on the cathode can be used as a measure of the Tl. Tervalent thallium can be determined volumetrically by means of EDTA (disodium salt). Excess of the reagent is back-titrated with standard $\text{Th}(\text{NO}_3)_4$ soln. Copper, Pb, Zn, Cd, Al, Fe, Ni, Co, Bi, Mn, F⁻, PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$ must be absent. In an absorptiometric estimation of Tl^{III} , the complex with Zn dibenzylthiocarbamate, which is stable in subdued light, is used. After extraction of the complex with CHCl_3 , the extinction of the soln. is measured at 430 m μ . Among the elements that interfere are Sb, Bi, Co, Hg, Ni and Ag. Univalent thallium can be determined by spectrophotometric titration with EDTA at 222 m μ , and by direct coulometric oxidation at 1.34 V vs. the S.C.E. in acid soln. In the latter instance the reaction is doubtless complex, as Lingane's equation is not obeyed. J. H. WATON

60. The chemical analysis of the rare-earth elements. XII. A polarographic study of neodymium. Seizo Misumi and Akio Iwase (Dept. of Chem., Faculty of Liberal Arts, Yamagata Univ., Koshirakawa-cho, Yamagata). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, 77 (4), 640-643.—The polarographic wave of Nd^{3+} was studied in tetramethylammonium chloride soln. (pH 3 to 5) and its use in analysis is discussed. The wave height ($E_{\frac{1}{2}} = 1.84$ V vs. the S.C.E.) is proportional to concn. ($< 10^{-3}$ M) at pH 3-8 in the presence of gelatin. No appreciable difference in the polarogram is observed for a mixed soln. of Pr and Nd, the wave height being proportional to their sum. K. SAITO

61. Spectrophotometric determination of cerium in carbonate solution. N. Conca and C. Merritt, jun. (Polytechnic Inst. Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1264-1268.—From 2 to 25 p.p.m. of Ce^{4+} can be determined to within ± 0.2 p.p.m. by measuring the extinction in 3 M aq. K_2CO_3 (pH 11 to 12) at 305 m μ in a 1-cm cell. Beer's law is valid for concn. of Ce > 40 p.p.m.; the extinction should not be recorded until the reading is constant. The standard deviation is 0.003 extinction unit. The sample is dissolved in dil. H_2SO_4 (Ce^{3+} are oxidised with $\text{K}_2\text{S}_2\text{O}_8$) before the final dilution to 50 ml with 3 M K_2CO_3 . The ions that interfere, viz. Br^- , NO_3^- , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , UO_2^{2+} , VO^{2+} , Fe^{3+} , Cu^{2+} and Y^{3+} should be eliminated initially. The method is an improvement on that in which H_2O_2 is used (cf. *Ibid.*, 1953, 25, 971). W. J. BAKER

62. Determination of cerium and chromium in cerium-chromium-uranium mixtures. C. V. Banks and J. W. O'Laughlin (Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1338-1340.—In the procedure described, Cr is first determined on an aliquot (≈ 2 to 50 mg of Cr) of the sample soln. (in dil. HCl or HNO_3) by preferential oxidation to Cr^{VI} with hot conc. HClO_4 (Ce is unaffected), followed by addition of an excess of Fe^{2+} and back-titration of the excess with 0.1 N $\text{Ce}(\text{SO}_4)_2$. The low values for Cr often obtained after an HClO_4 oxidation are ascribed to the reduction of Cr^{VI} by Cl^- . The soln. should be cooled and diluted immediately after oxidation. Sodium bicarbonate (2 to 3 g) is then added and the soln. is boiled. This reduces the acidity, and the liberated CO_2 helps sweep out Cl from the soln. Cerium and Cr are then determined in another aliquot by complete oxidation of both with boiling peroxy-disulphuric acid in the presence of AgNO_3 ,

followed by addition of excess of Fe^{2+} to the cool diluted soln. and back-titration with $\text{Ce}(\text{SO}_4)_2$. The error is ± 0.04 mg for Cr concn. > 30 mg and ± 0.3 mg for Ce concn. of ≈ 200 mg. The method is applicable to U-Cr-Ce alloys, but the ratio of Ce to Cr should be large. W. J. BAKER

63. Detection of carbon in spot analysis. F. Feigl and D. Goldstein (Min. Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1956, (7-8), 1317-1321.—Although the CO_2 -limewater test devised by Emich for the detection of C is sensitive down to 0.01 μg , it has limited application, e.g., when testing for inclusions of C in rocks, for bitumen and humus in soils, or in the testing of mineral dust or water residues for organic traces, because it necessitates the absence of carbonates. Two generally applicable, although less sensitive, spot tests are described which depend on the redox reactions that occur when dry mixtures containing C or organic compounds are heated with KIO_3 or MoO_3 , resulting in the formation of KI and molybdenum blue, respectively. These two reaction products are easily recognised. *Procedure*—(i) Place a test fragment in a micro test-tube with a few centigrams of KIO_3 . Add one or two drops of H_2O and stir. Evaporate to dryness. Cover the residue with a little powdered KIO_3 and heat at 300° to 400° in an electric furnace. Cool, add one drop of starch soln. and one drop of H_2SO_4 (1:1). A blue coloration indicates a positive result. Conduct a blank test on the KIO_3 . Identification limits (relative to C) are 0.5 to 6 μg . (ii) Place a test fragment or evaporate one drop of soln. in a hard-glass tube (75 mm \times 7 mm) having one end closed. Half fill with finely powdered MoO_3 . Evacuate the tube with a suction pump and seal with a pinch clip. Heat for 1 to 2 min. in a small flame in such a way that the upper layer of MoO_3 is heated first and then the lower layer. The presence of combustible material is indicated by the appearance of a blue zone in contact with the bright-yellow MoO_3 ; the zone varies in size and intensity according to the amount of C or organic matter present. A blank test on the MoO_3 is advisable. Identification limits are from 1 to 8 μg . Inorganic reducing compounds must be absent in both tests. Prior removal of S, SO_2 and compounds of Fe^{II} , etc., is easily accomplished by evaporation of the sample with H_2O_2 . D. F. PHILLIPS

64. Paper chromatography of oligosilicic acids. H. Baumann (Chem. Abt. Silikose Forschungsinst., Bochum, Germany). *Naturwissenschaften*, 1956, 43 (13), 300-301.—A soln. of SiO_2 , adjusted to a pH of approx. 3 by the addition of acetate or citrate buffer, is chromatographed in a moist chamber (the spot must not be dried on the paper) with a solvent mixture of isopropyl alcohol-acetic acid-water (20:2:5). At least four spots are seen on the chromatogram. Silicic acid has an R_F of 0.75 and three distinct silicic acids of higher mol. wt. have R_F values between 0.75 and 1.0. After the paper has been dried, the spots are located with a spray soln. of ammonium molybdate, buffered to a pH of 1.5. The paper is allowed to hang in a moist chamber overnight, during which time the molybdate hydrolyses the silicic acids of higher mol. wt. Condensed silicic acids do not react unless the paper has been treated with dilute NaOH before the molybdate reagent is applied. The molybdosilicate complex is strongly adsorbed on the paper and can be made visible by inspection in u.v. light; alternately, the molybdenum-blue complex can be formed

by reduction with hydrazine sulphate and treatment with ammonia. The reagent is sensitive down to $0.2 \mu\text{g}$ of SiO_2 per sq. cm. E. KAWERAU

65. Photometric determination of germanium with "phenylfluorone." C. L. Luke and M. E. Campbell (Bell Telephone Lab., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1273-1276.—Not more than $40 \mu\text{g}$ of Ge can be determined, in the presence of milligram amounts of other metals, by isolating Ge by one extraction with CCl_4 from a $9 N$ HCl soln. and then measuring the extinction of the Ge complex with "phenylfluorone" at $510 m\mu$ in a 1-cm cell. Very rapid development of the colour is achieved by adjusting the soln. to pH 3.1 before adding the reagent. Tervalent As is extracted with Ge but does not interfere. Since the max. recovery of Ge is only 95%, the extraction procedure should be included in the preparation of the calibration curve. Unless effectively removed, Sb, Cr and Ti (especially if present with Fe) cause low results. The sample is usually heated to fuming with H_2SO_4 or HClO_4 and is then diluted before extraction with CCl_4 ; if $> 0.25 \text{ mg}$ of Sb^{V} is present this must be reduced to Sb^{III} with hydrazine sulphate before dilution. The use of complexing agents to prevent interference by small concn. of other metals is discussed (cf. Schneider and Sandell, *Mikrochim. Acta*, 1954, 263).

W. J. BAKER

66. Determination of traces of gallium and indium in germanium and germanium dioxide. C. L. Luke and M. E. Campbell (Bell Telephone Lab., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1340-1342.—In the photometric determination of 1 to 10 p.p.m. of Ga or In in Ge or GeO_2 , the Ge is removed by distillation as GeCl_4 . The determination of Ga in the residue can be made by one ether extraction from 6 to $6.5 N$ HCl , followed by one oxine- CHCl_3 extraction from an alkaline soln. of NaCN and measurement of the extinction of the yellow coloration of the final extract at $400 m\mu$ in a 5-cm cell. Since the max. recovery of Ga is only 95%, the ether extraction should be included in the procedure for the preparation of the calibration curve. The determination of In in the distillation residue can be made by several extractions with dithizone- CHCl_3 from an alkaline soln. of NaCN , followed by an oxine- CHCl_3 extraction from an aq. buffer soln. at pH 3.5, and measurement of the extinction of the yellow extract at $400 m\mu$. Bismuth can be removed by a dithizone extraction from HClO_4 soln. (1 + 9) before the extraction from alkaline cyanide, and Sn^{II} should be converted into Sn^{IV} to prevent its extraction by dithizone. Very low values for In are obtained if 0.1 mg of either Rh or Ir is present, and $> 0.1 \text{ mg}$ of Be also gives low values. In the procedure for Ga, interference by Mo is prevented by a small addition of $\text{Pb}(\text{NO}_3)_2$ just before the oxine extraction; any Ti present should be reduced to Ti^{II} . The results are highly accurate.

W. J. BAKER

67. Photometric determination of tin with "phenylfluorone." Determination of tin in lead and one per cent. antimony-lead alloys. C. L. Luke (Bell Telephone Lab., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1276-1279.—In the procedures described the bulk of the interfering metals is removed from the sample soln. by standard chemical methods and, after separating or complexing the small amounts of interfering ions that still remain, the Sn^{2+} are isolated finally by

two extractions with a freshly prepared 1% (w/v) soln. of diethylammonium diethyldithiocarbamate (I) in CHCl_3 . The Sn is then determined spectrophotometrically in the extract, at exactly pH 1.8, by the "phenylfluorone" method as used for Ge (cf. *Anal. Abstr.*, 1957, **4**, 65), the extinction being measured at $510 m\mu$ in a 1-cm cell. For samples containing Pb, the Sn should be separated by co-pptn. with MnO_2 from HClO_4 - HNO_3 soln. (Fe and Bi also ppt., but not Cu). The isolation of the Sn after its initial separation from the sample soln. is discussed in respect of the particular sample. A modification of Wyatt's method (cf. *Analyst*, 1955, **80**, 368) is preferred. Quadrivalent Sn is reduced to Sn^{II} with thioglycolic acid; As and Sb are selectively reduced to the tervalent state with hydrazine sulphate; Fe^{III} is reduced to Fe^{II} with KI-ascorbic acid at 50° . Small amounts of Mo in the second extract are complexed with H_2O_2 . With some samples it may be necessary to separate Sn still further by an acid sulphide pptn. or cupferron extraction (or both) before proceeding with the double extraction with I, but this cannot be done if Ta and P are present. The accuracy is high for concn. of Sn of 20 to $80 \mu\text{g}$ in Pb and in 1% Sb-Pb alloys. W. J. BAKER

68. Rapid determination of tin in tin-lead alloy. Koichi Emi and Tadashi Hayami (Chem. Dept., Fac. of Sci., Okayama Univ., Tsushima, Okayama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (12), 960-961.—The gravimetric determination of Pb and Sn in their binary mixtures was studied with ammonium oxalate (I) as masking agent. The sample (Sn, 1 to 50%) is dissolved in a mixture of HNO_3 and HCl (1 + 3) (20 ml) and water (50 ml), and treated with I (> 10 times the weight of the sample) and aq. NH_3 soln. until a faint turbidity is observed. This product is acidified to a concn. of $0.2 N$ HCl , filtered and washed with a 1% I soln. The filtrate is treated with I (> 5 times the weight of the sample), then with H_2S for the pptn. of Pb as PbS , and again filtered. The filtrate is made ammoniacal to convert all the Sn into thiostannate, and boiled with H_2O_2 (30%, 25 ml). The pptd. SnO_2 is ignited and weighed. Lead oxalate and sulphide are converted into sulphate and determined gravimetrically. K. SAITO

69. A precipitation-chromatographic method for the determination of lead. A. F. Nedobora. *Sbornik Stud. Rabot. Mosk. Tekhnol. Inst. Ref. i Moloch. Prom-sti.*, 1955, (3), 100-103; *Ref. Zhur., Khim.*, 1955, Abstr. No. 52,162.—The column is packed with a mixture of anhyd. Al_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ (1 ml of N $\text{K}_2\text{Cr}_2\text{O}_7$ to 10 g of Al_2O_3). To prepare a graph of the dependence of zone height in millimetres on the concn. of Pb^{2+} in mg per ml, standard soln. of Pb^{2+} are prepared, of concn. 1 to $0.0001 N$. Through the column is passed 1 ml of each $\text{Pb}(\text{NO}_3)_2$ soln., and the height of the zone formed is measured. The sensitivity of the method is 0.99 mg of Pb^{2+} per ml. At different H^+ concn., the height of the zone at a given concn. of Pb^{2+} will vary; therefore the soln. must first be neutralised. The presence of each of the following cations— Ba^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} , Ca^{2+} , K^+ , Na^+ , Hg^{2+} , Hg^+ , Sr^{2+} , Zn^{2+} , Bi^{3+} and Cr^{3+} —in a 20-fold excess over the concn. of Pb^{2+} has no influence in most cases, but in the presence of the coloured cations Ni^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} and Cu^{2+} , the colour of the zone takes on a shade corresponding to the given cation. The presence of Hg^{2+} and Hg^+ affects the height of the zone, since Hg^{2+} and Hg^+ form ppt. with CrO_4^{2-} .

the solubilities of which are little different from that of PbCrO_4 . The presence of Bi^{3+} also increases the zone height. The deviation of results between this and the gravimetric determination of Pb^{2+} is $> 3\%$. The described method is simple and requires only a small quantity of soln. (> 4 ml). The time for a determination is 15 to 20 min.

C. D. KOPKIN

70. Chemiluminescent indicator titration of lead with potassium chromate in lead-tin alloys and in metallic samples containing lead, tin, antimony and arsenic. F. Kenny and R. B. Kurtz (Hunter Coll., New York, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1206-1207.—Tin interferes in the titration of Pb with K_2CrO_4 with siloxene as a chemiluminescent indicator (*Anal. Abstr.*, 1954, **1**, 458). However, satisfactory results are obtained when Sn is volatilised as its bromide before the titration. The removal of Sb and As can be effected similarly.

J. H. WATON

71. An apparatus for the reduction, storage and titration of salts of tervalent titanium. N. Kh. Pinchuk. *Nauch. Byull., Leningrad Univ.*, 1955, (33), 24-27; *Ref. Zhur., Khim.*, 1955, Abstr. No. 52,126.—The apparatus for the production, storage and titration of a soln. of Ti^{3+} consists of a three-necked flask of capacity 500 to 800 ml, painted black or with paper glued on to it. To the flask is joined a separating funnel of capacity 300 to 500 ml in which are several glass beads, a little glass wool and a layer of metallic Zn or Cd almost to the neck; a flask of capacity 2 to 3 litres; a siphon of 2 to 3 mm diam. and a burette with a side-tap and with a side-arm fused in the top for the exit of gas, with a Bunsen valve closed by a glass tube with a rubber bung, which is removed when reducing Ti^{4+} and filling the burette. Having assembled the apparatus, pass CO_2 or H for 30 to 40 min. Fill the funnel three-quarters full with a soln. of Ti^{4+} , then run the reduced soln. into the three-necked flask and determine its concn. The burette is filled by increasing the gas pressure in the three-necked flask (i.e., by raising the flask which contains water). It may be used for the production, storage and titration of soln. of Cr^{2+} .

C. D. KOPKIN

72. Photometric determination of chlorine in metallic titanium. Iwaji Iwasaki, Takashi Tashiro and Takejiro Ozawa (Dept. of Anal. Chem., Tokyo Inst. Technol., Okayama, Tokyo). *Japan Analyst*, 1956, **5** (5), 275-279.—The rapid (60 to 80 min.) determination of Cl ($> 0.01\%$) in Ti was studied with a mixed reagent of iron alum and $\text{Hg}(\text{SCN})_2$ (cf. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1952, **73**, 835). Chloride reacts with $\text{Hg}(\text{SCN})_2$ to produce free SCN^- , which give a red colour with Fe^{3+} and HgCl_2 . Procedure—The sample (0.1 g) is fused with NaOH (1.0 g), dissolved in water, and centrifuged, and the supernatant liquid is neutralised with 70% HClO_4 (2.7 ml). The neutral soln. (10 ml) is treated with iron alum (6% in 70% HClO_4 , 2 ml) and ethanolic $\text{Hg}(\text{SCN})_2$ (0.03%, 1 ml), and the resulting colour is measured at 460 μm . The working curve is not linear, but is reproducible for $< 250 \mu\text{g}$ of Cl per 10 ml. The sample can also be decomposed with KOH or HF.

K. SAITO

73. Amperometric determination of zirconium with 1-nitroso-2-naphthol. R. F. Wilson and T. Rhodes (Texas Southern Univ., Houston, U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1199-1200.—The amperometric titration of Zr with 1-nitroso-2-naphthol gives accurate results, the relative error being $\pm 0.4\%$.

A tenfold excess of F^- gives no interference, but larger amounts cause a high vol. of titrant. Besides Cu, Co, Fe and Pd, which are known to form ppt. with the reagent, Ni is the only one of the ions studied that causes interference when present in small amounts. The 1-nitroso-2-naphthol reagent is stable for \approx two weeks.

J. H. WATON

74. The determination of sulphate in thorium nitrate. J. Clinch (Thorium Ltd., Uphall Rd., Ilford, Essex, England). *Analyst*, 1956, **81**, 358-362.—A new method is described for the determination of SO_4^{2-} in $\text{Th}(\text{NO}_3)_4$. The sample (10 g) is applied to a column of Zeo-Karb 225 (H) resin previously treated successively with dil. HCl and water and is washed through the column with water. The eluate is evaporated almost to dryness with Na_2CO_3 and then twice with conc. HCl. After addition of conc. HCl and water the boiling liquid is treated with boiling BaCl_2 soln., the mixture is kept hot for 1 hr. and set aside overnight. The pptd. BaSO_4 is then collected and ignited at 900° to constant wt. Another method is described in which the Th is removed as its oxalate and SO_4^{2-} are determined in the supernatant liquid by the same pptn. procedure. This method tends to give lower results than the elution method owing to co-pptn. of SO_4^{2-} with the oxalate. By the procedure described for the evaporation and for the pptn. of BaSO_4 , adsorption of NO_3^- on the ppt. is prevented. Recovery of added SO_4^{2-} is complete within the limits of experimental error.

A. O. JONES

75. The elimination of the distillation procedure in the Kjeldahl method. R. Belcher and M. K. Bhaty (Univ. Birmingham, England). *Mikrochim. Acta*, 1956, (7-8), 1183-1186 (in English).—By application of the hypochlorite titration of Kolthoff and Stenger (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 79) the distillation process in the Kjeldahl method can be eliminated. Mercury serves as catalyst; other catalysts tried interfered in the titration, either because of their colour masking the end-point or because they reacted with the titrant. Satisfactory results were obtained on both the micro and semi-micro scale for a limited number of compounds. On the micro scale, digestion and titration can be done in the same vessel, but on the semi-micro scale the digestion should be transferred to a suitable titration vessel. Direct titration is inapplicable when pre-reduction has to be used, as all reagents tested interfered with the end-point.

D. F. PHILLIPS

76. The analysis of cyanogen compounds. IV. Spectrophotometric determination of ammonia with phenol and hypochlorite. Shinsuke Takei (Dept. of Applied Chem., Faculty of Eng., Tōhoku Univ., Katabira-cho, Sendai). *Japan Analyst*, 1956, **5** (5), 261-264; *Technol. Rep. Tōhoku Univ.*, 1955, **20**, 71-76 (in English).—The determination of NH_3 by the colour reaction with phenol and ClO^- (Riley, *Anal. Chim. Acta*, 1953, **9**, 575) was modified for use in the determination of NH_3 in KOCN. A neutral sample soln. is mixed with an ethanolic soln. of phenol (0.25%, 1 ml), 5N NaOH (1 ml) and NaClO (3 ml, containing $\approx 2.5\%$ of available Cl). The extinction is measured after 5 to 10 min. at 625 μm . The working curve is linear for 0.2 to 6 p.p.m. and the error is $< 1.5\%$. The presence of CN^- (> 0.1 mg) and SCN^- ($> 50 \mu\text{g}$) vitiates the estimation. The analysis must be carried out without application of heat to avoid decomposition of OCN $^-$.

K. SAITO

77. **A rapid method for the determination of a small amount of nitrogen dioxide in liquid oxygen in air separators.** Yoshitaka Kobayashi and Tetsuzo Kitagawa (Fac. of Eng., Yokohama Univ., Minami-ku, Yokohama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (9), 651-654.—For the determination of 10 to 500 p.p.m. of NO_2 in oxygen (gas and liquid) a detector tube was devised (limit of detection 0.1 p.p.m.) and its use studied. Silica gel (20 to 40 mesh) is impregnated with *o*-tolidine hydrochloride (0.05% *o*-tolidine in dil. HCl containing ethanol) and packed in a glass tube (diam. 3 mm; length 60 to 80 mm). The sample is placed in a flask and evaporated until all O is removed; no appreciable loss of NO_2 is observed. Air is then passed in to displace NO_2 into the detector (rate of flow, 100 ml per 25 sec.), and the length of the resulting coloured layer is measured. The content of NO_2 is calculated from an empirical table. The average deviation from the mean is $\approx 5\%$ (relative). K. SAITO

78. **The determination of very small quantities of nitrite.** H. Zimmer (Mehringdamm 53, Berlin, Germany). *Z. anal. Chem.*, 1956, **151** (4), 258-262.—The method is based on the diazotisation of *p*-nitroaniline hydrochloride and coupling with 1-naphthylamine in strongly acid solution to give a red azo dye. From 20 to 60 μg per litre can be estimated. Nitrate, HNO_3 in concn. $< 2\text{ N}$, Fe^{3+} in concn. $< 20\text{ mg}$ per litre (the addition of NaF prevents interference from Fe present in greater concn.), alkali metals, alkali earths and phenol in concn. $< 13\text{ mg}$ per litre do not interfere; heavy metals interfere because of their colour, and strong reducing agents, e.g., SnCl_2 and Na_2S , must be absent. To 100 ml of test soln. (containing $\approx 20\text{ }\mu\text{g}$ of NaNO_2), add 0.2 ml of reagent solution (0.5 g of *p*-nitroaniline hydrochloride and 0.7 g of 1-naphthylamine dissolved in 100 ml of methanol) followed by conc. H_2SO_4 (1 ml). Determine the extinction after 15 min. Good agreement with the classical method is obtained. P. S. STROSS

79. **A selective spot test for nitrate ion.** H. A. Suter and P. H. Suter (Rollins College, Winter Park, Florida, U.S.A.). *Mikrochim. Acta*, 1956, (7-8), 1136-1139 (in English).—The diphenylamine test for NO_3^- may be made selective by reducing the oxidising agents present with Na_2SO_3 . In the presence of NO_2^- , Na_2SO_3 reduces NO_3^- to NO_2^- ; this is overcome by first destroying NO_2^- with NaN_3 . **Procedure**—Add a few mg of NaN_3 to a drop of test soln. in the depression of a white spot-plate. Add two drops of 6 *M* H_2SO_4 . When gas evolution ceases add a few mg of solid Na_2SO_3 then two drops of 6 *M* H_2SO_4 . Stir and add five to ten drops of diphenylamine. The formation of a blue colour indicates the presence of NO_3^- . **Preparation of reagent**—Add NH_4Cl (250 g) to H_2O (90 ml). Add a cooled soln. of 250 mg of diphenylamine in conc. H_2SO_4 (100 ml) to the NH_4Cl soln. and make up to 250 ml with conc. H_2SO_4 . With this method, 0.5 μg of NO_3^- can be detected in the presence of 500 μg of H_2O_2 , NO_2^- , ClO_3^- , BrO_3^- , $[\text{Fe}(\text{CN})_6]^{3-}$, CrO_4^{2-} , MnO_4^- , VO_3^- , MoO_3^{2-} , WO_4^{2-} , Fe^{3+} and Ce^{4+} . D. F. PHILLIPS

80. **Analytical applications of spectrophotometry of the system $\text{Cr}_2\text{O}_7^{2-}$ - 2Cr^{3+} .** II. Quantitative determination of hydrazine. F. Capitán García and M. Lachica Garrido (Zaidan Exp. Sta., Granada, Spain). *An. Real Soc. Españ. Fis. Quím., B*, 1956, **52** (4), 251-256.—The use of $\text{K}_2\text{Cr}_2\text{O}_7$ as the

reactive agent for the spectrophotometric determination of hydrazine is proposed. A study is made of the various factors that influence the determination, particularly the order of adding the reagents, the concn. of H_2SO_4 used, and the stability of the solutions. Under the conditions employed, no errors are observed in the method. Previous work on the methods of determining hydrazine is briefly reviewed. C. A. FINCH

81. **Extraction method for colorimetric determination of phosphorus in microgram quantities.** N. S. Ging (Univ. of Kansas Medical Center, Kansas City, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1330-1333.—Ways of increasing the accuracy of the standard colorimetric procedures for the micro-determination of P, especially in biological samples, are reported. Conversion of P into molybdophosphoric acid and subsequent development of the molybdenum-blue complex, either in the aq. phase at pH 4 or in *n*-butanol at pH 2, eliminates serious interference from the chief inhibitory ions (F^- , AsO_3^{3-} , acetate, citrate and oxalate), besides preventing hydrolysis of acid-labile phosphates. If 2% quinol soln. is used as the reducing agent, greater colour stability is ensured, the final acid concn. can be as low as 0.04 *N* (so that the non-specific blue colour does not appear), and no heating is required. The extinction is measured at 720 $m\mu$ in a 1-cm cell. The accuracy is within $\pm 2\%$ and the lower limit of sensitivity is $\approx 0.5\text{ }\mu\text{g}$ of P per ml. Procedures for use in the presence of labile phosphates or major inhibitory ions, and in the absence of either of these, are given. W. J. BAKER

82. **Radioactivation analysis of phosphorus in iodine.** J. A. James and D. H. Richards (Res. Lab., British Thomson-Houston Co., Ltd., Rugby, England). *Nature*, 1956, **177**, 1230.—Phosphorus present in silicon prepared for semiconductor devices by the silicon iodide process is introduced as an impurity in the iodine used. The phosphorus content of iodine, which varied from 10 to 0.1 p.p.m., was estimated as phosphate by radioactivation analysis as described by James and Richards (*cf. Anal. Abstr.*, 1955, **2**, 2081). Details are given of the irradiation of the iodine in a thermal neutron flux. The whole process takes eight days and is 70 to 80% efficient, detecting $< 0.003\text{ p.p.m.}$ in 1 g. E. G. CUMMINS

83. **Use of paper chromatography for differential analysis of phosphate mixtures.** E. Karl-Kroupa (Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1091-1097.—Quantitative procedures are given for the analysis of phosphate mixtures containing ortho-, pyro- and tri-phosphates, long-chain phosphates and ring phosphates by ascending chromatography. Both one- and two-dimensional techniques are described; in the two-dimensional techniques, basic and acid solvents are used either at right angles to each other or in opposite directions. At all times parallel runs with reference soln. must be employed. When basic and acid solvents are used at right angles, pyrophosphate can be employed as an internal reference standard for dividing the long-chain phosphates from the ring phosphates. The rapid quant. determination involves cutting out the zones and completing the analysis colorimetrically. For accurate work, correction factors are applied to take into account hydrolysis, particularly with the triphosphate. The methods are applied to the

analysis of commercial sodium triphosphate, synthetic detergent mixtures and waters.

J. H. WATON

84. Determination of soluble phosphate and total phosphorus in sea water and of total phosphorus in marine muds. J. D. Burton and J. P. Riley (The University, Liverpool, England). *Mikrochim. Acta*, 1956, (9), 1350-1365 (in English).—Metol at 100° has been investigated as a reagent for the reduction of molybdophosphoric acid in the determination of phosphate in sea water. It is found to have several advantages over SnCl_2 for this purpose. The molybdenum-blue colour is stable for several hours and the calibration curve is not dependent on the batch of reagent. Beer's law is obeyed up to 1 mg of phosphate phosphorus per litre. The method has about 30% greater sensitivity than the SnCl_2 method. Arsenic does not interfere, nor do Fe and Cu in moderate amounts. The total P in sea water and marine muds is determined by evaporating the sample to dryness with a mixture of nitric and perchloric acids and determining the inorganic phosphate colorimetrically.

C. A. SLATER

85. Use of complexones in chemical analysis. XLVI. Gravimetric and volumetric determination of arsenic. M. Malinek and B. Rehák (Metallurgical Lab., Czech. Acad. Sci., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, 21 (3), 777-779 (in English).—To determine As gravimetrically or volumetrically, after pptn. as $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, bivalent cations are screened by adding EDTA (disodium salt), and ter- and quadri-valent cations by adding 1:2-dihydroxybenzene-3:5-disulphonic acid (tiron). The minimum amount of the tiron must be used, otherwise low results are obtained. The ppt. is either (i) ignited and weighed as $\text{Mg}_2\text{As}_2\text{O}_7$, or (ii) dissolved in conc. HCl and nearly neutralised; excess of standard EDTA is added, the pH is adjusted with alkaline buffer and the soln. is back-titrated with 0.1 M MgCl_2 with Eriochrome black T as indicator. An alternative procedure is to dissolve the ppt. in conc. HCl, reduce the arsenate by the addition of hydrazine sulphate and KBr, and titrate the Mg with EDTA after adjusting the pH.

P. S. STROSS

86. Colorimetric method for the quantitative determination of antimony in minerals. E. Popper, I. Olteanu, H. Popescu and G. Suciu (Fac. de Farm., Univ. 'V. Babes', Cluj, Roumania). *Rev. Chim.*, Bucharest, 1956, 7 (6), 367-369.—A method is described whereby Sb is separated directly as SbOCl after evaporating the sample first with HNO_3 , and secondly with HCl. The determination of Sb is completed colorimetrically with thiourea. The method is rapid and should find applications in the pharmaceutical as well as in the metallurgical fields.

J. H. WATON

87. Photometric determination of antimony in tin and tin-lead solder with rhodamine B. W. C. Coppins and J. W. Price (Tin Res. Inst., Greenford, Middx., England). *Metallurgia, Manchester*, 1956, 53, 183-184.—The sample (tin or tin-lead solder) (0.5 g) is heated with 10 ml of conc. H_2SO_4 , cooled, diluted with 30 ml of water, again cooled, and 50 ml of conc. HCl is added. The soln. is then made up to 100 ml and, to a 10-ml aliquot, 0.5 ml of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (1% aq.) is added. The soln. is cooled to below 25° and 3 ml of $\text{Ce}(\text{SO}_4)_2$ soln. (3.3 g in 100 ml of $\text{N H}_2\text{SO}_4$), followed by 0.5 ml of hydroxylamine hydrochloride soln. (1% aq., fresh), is added.

When reduction of Sb^{V} to Sb^{III} is complete, the solution is diluted to 60 ml, 10 ml of isopropyl ether is added and the liquid layers are separated. The isopropyl ether fraction is washed twice with 2 ml of N HCl , and 2 ml of rhodamine B soln. (0.02 g in 100 ml of N HCl) is added. The extinction is measured in a spectrophotometer with a 1- or 2-cm cell at 550 μ . Calibration is carried out with pure Sb.

S.C.I. ABSTR.

88. Determination of metals with standard solution of potassium ferrocyanide. IX. Determination of bismuth. Yoshio Fujita (Dept. of Applied Chem., Faculty of Eng., Osaka Univ., Miyakojima-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, 77 (4), 615-619.—Experimental conditions for the titration of Bi with $\text{K}_4\text{Fe}(\text{CN})_6$ in an acid soln. were studied in the presence of KI and glycerol. Satisfactory results were obtained at pH 1.6 when the titration was carried out very slowly (5 sec. per drop).

K. SAITO

89. Determination of niobium in the presence of tantalum, tungsten, molybdenum, titanium and other components of stainless steels. S. Vivarelli. (Anal. Chem. Inst., Univ., Florence, Italy). *Chim. e Ind.*, 1955, 37 (13), 1026-1028.—The sample (0.5 to 2.0 g) is dissolved in HClO_4 (20 to 60 ml) when the Nb precipitates as niobic acid. The ppt. is dissolved by fusion with Na_2CO_3 followed by saturation of the sodium niobate soln. with HCl gas. The Nb is determined in the soln., after adding ethanediol (5 ml), polarographically by means of the cathodic wave, when Nb appears at $E_{\frac{1}{2}} = -0.395$ V. Results are tabulated which indicate an accuracy within $\pm 2\%$.

C. A. FINCH

90. Tri(hydroxymethyl)aminomethane as standard alkali in acidimetric combustion method for determining sulphur. A. C. Holler (Twin City Testing and Engng Lab., St. Paul, Minn., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1359.—Tri(hydroxymethyl)aminomethane is suitable as the standard alkali in the determination of S. The solid can be prepared with high purity; its hygroscopicity is comparable to that of common primary standards; the compound and its soln. do not absorb CO_2 from the air; and the pH of its equivalence point is 4.7, comparing favourably with the end-point of pH 5.3 taken in the acidimetric combustion method.

G. P. COOK

91. Determination of sulphide sulphur in minerals. A. R. Vasudeva Murthy, V. A. Narayan and M. R. A. Rao (Indian Inst. Sci., Bangalore, India). *Analyst*, 1956, 81, 373-375.—An accurate and rapid method for the determination of sulphide sulphur in the presence of sulphates is described and the simple apparatus is illustrated. The mineral is treated with HI ($\text{KI} + \text{HCl}$) and the liberated H_2S is carried by a stream of H or N into a suspension of $\text{Cd}(\text{OH})_2$ ($\text{Cd acetate} + \text{NaOH}$). The absorbing liquid is then acidified with acetic acid containing a known amount of standard I soln. and the unused I is titrated with $\text{Na}_2\text{S}_2\text{O}_3$. Free S and SO_4^{2-} do not interfere. The method is applicable also to the determination of sulphide in Ag_2S , NiS and CoS , but not in pyrites and chalcopyrites.

A. O. JONES

92. Analytical applications of spectrophotometry of the system $\text{Cr}_2\text{O}_7^{2-}-2\text{Cr}^{3+}$. I. Study of the factors affecting the determination of Cr^{3+} . F. Capitán García and M. Lachica Garrido (Zaidin

Exp. Sta., Granada, Spain). *An. Real Soc. Españ. Fis. Quím.*, B, 1956, **52** (4), 237-250.—The characteristics of the spectrum of $\text{Cr}_2(\text{SO}_4)_3$ are verified, the effect of the presence of H_2SO_4 and H_3PO_4 being determined. A study is also made of the effect of temp., stability of the soln., the limits between which Beer's law is obeyed, interference by other ions, the effect of excess of $\text{K}_2\text{Cr}_2\text{O}_7$, and the accuracy of the method. In the determination of Cr^{3+} , a max. error of $\approx 5\%$ is observed. Experimental methods and a range of typical results are detailed. C. A. FINCH

93. Separation and identification of molybdenum and tungsten. L. C. F. Blackman (Admiralty, Harlow, Essex, England). *Mikrochim. Acta*, 1956, (9), 1366-1368 (in English).—An aqueous solution containing W and Mo (as tungstate and molybdate) (1 drop containing $1.5\ \mu\text{g}$ of each) is placed on Whatman No. 40 filter-paper (5.5 cm) and ringed with 30% aq. quinine hydrochloride. The whole spot is then treated with the quinine reagent. The paper is placed in a ring oven (Weisz) and washed with 0.1 N HCl. After drying the paper over a hot-air blower, the centre portion (1 cm in diam.) containing the precipitated tungsten is punched out. The Mo in the ring zone is identified by spraying with a freshly prepared soln. of KSCN (10%) and SnCl_2 (5%) in 3 N HCl. A brick-red ring of tervalent molybdenum thiocyanate is formed. The punched-out centre of the paper is placed on a second paper and washed with 0.1 N aq. NH_3 . The paper is developed by immersion in 0.1% rhodamine-B solution in 6 N HCl and washing under running water. A violet ring of the tungsten complex is formed. C. A. SLATER

94. Rapid polarographic determination of uranium in non-aqueous solvents. D. J. Fisher and P. F. Thomason (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1285-1288.—In the rapid and accurate procedure described, the U^{VI} is almost completely ($\approx 99.9\%$) separated from the sample soln. by extraction into 5 to 30% (v/v) tributyl phosphate in isopropyl ether. The presence of HNO_3 in the aq. phase is unnecessary. If the sample soln. is very radioactive, a 5% soln. of tributyl phosphate is an effective extractant for U, giving decontamination factors of ≈ 100 . The organic phase is diluted with glacial acetic acid to a concn. of $\approx 50\ \mu\text{g}$ of U per ml, and is then adjusted to 0.25 M with LiClO_4 (solid salt) as supporting electrolyte. This soln. is then polarographed, with the instrument described by Kelley (*Ibid.*, 1952, **24**, 1895); well-defined U waves are obtained at an apparent $E_{\frac{1}{2}}$ of $\approx -0.2\ \text{V}$ vs. the S.C.E. In an alternative but less satisfactory method of preparing the extract of U for polarographic analysis, the organic soln. is shaken with an equal vol. of Cu-free H_2O , the separated aq. phase is heated for 3 min. (hot-plate), cooled and adjusted to 0.1 M in HNO_3 . After dilution to a U concn. of $\approx 50\ \mu\text{g}$ per ml, the soln. is polarographed. The aq. phase must be heated, otherwise a double, complex wave is obtained. W. J. BAKER

95. Automatic oximetric micro-method for uranium. K. A. Allen (Oak Ridge Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1144-1147.—Amounts of U from 10 to 100 μg in H_2SO_4 soln. are estimated by an automatic oximetric titration with 0.1 M $\text{Ce}(\text{SO}_4)_2$. The U is first reduced with Cr^{II} soln. and, after allowing aerial oxidation of U^{III} and excess of Cr^{II} , an excess

of standard Fe^{III} soln. is added, and the Fe^{II} is determined with the $\text{Ce}(\text{SO}_4)_2$. The vol. of titrant is obtained from the chart of a recording potentiometer. Although the procedure has been developed on pure soln. of U, it is probably still applicable in the presence of other ions that are not reduced by Cr^{II} , or that can be removed. Chloride and NO_3^- should be removed by evaporation with H_2SO_4 , and the effect of PO_4^{3-} is overcome by raising the acidity from M to 4 or 5 M H_2SO_4 . J. H. WATON

96. Isolation and measurement of uranium at the microgram level. C. L. Rulfs, A. K. De and P. J. Elving (Dept. of Chem. and Engng Res. Inst., Univ. of Mich., Ann Arbor, U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1139-1143.—Uranium is separated by a method in which two extractions with cupferron are used. The aq. soln. of the sample containing U^{VI} is extracted with cupferron in ether or CHCl_3 to remove other elements. The U is then reduced at a mercury cathode to U^{IV} or U^{III} , extracted as its cupferrate and finally re-extracted into 7 M HNO_3 . For U at the milligram level, the determination is completed photometrically; the technique gives a recovery of $\approx 94\%$. For U at the microgram level, a tracer technique with ^{235}U is used. The recovery is only $\approx 86\%$, but there is a 6% loss during the electro-deposition step previous to the α -particle count. When the sample contains fission products, the recovery is $\approx 85\%$, only 0.9% of the α -activity of the fission products causing contamination. A simple apparatus is described in which pre-extraction, simultaneous reduction and extraction, and re-extraction can be carried out. J. H. WATON

97. Potentiometric determination of uranium with ferric sulphate in an inert atmosphere. R. Fernández Cellini and J. Alonso López (Junta de Energía Nuclear, Spain). *An. Real Soc. Españ. Fis. Quím.*, B, 1956, **52**, 163-168.—The U ($< 5\ \text{mg}$) as aq. uranyl sulphate is reduced in a column of cadmium sponge and determined potentiometrically by oxidation in 0.1 N H_2SO_4 medium with aq. $\text{Fe}_2(\text{SO}_4)_3$ at room temp. in an inert atmosphere. A suitable apparatus is described. The method is applicable to uranite minerals provided that PO_4^{3-} are removed, e.g., by means of a column of cation-exchange resin (Amberlite IR-120). L. A. O'NEILL

98. Rapid determination of uranium in sea and river water. J. Korkisch, A. Thiard and F. Hecht (II Chem. Lab., Univ., Vienna, Austria). *Mikrochim. Acta*, 1956, (9), 1422-1430.—Two methods have been developed in which the U, after separation by ion exchange, is directly determined by polarography. River water is passed through a column of Amberlite IRA-400 (acetate form) and sea water through the resin in its chloride form. The resulting uranyl acetate and uranyl chloride ions are retained quantitatively in the pH ranges 3 to 9 and 4.25 to 5.25, respectively, and, after washing the resin with buffer (pH 5) and water, the U is eluted with 0.8 N HCl and determined polarographically. The uranium content of 1 litre of water can be determined in 8 hr. with an accuracy within $\pm 15\%$. C. A. SLATER

99. The determination of small amounts of uranium in rocks and natural waters. F. Hecht, J. Korkisch, R. Patzak and A. Thiard (II Chem. Lab., Univ., Vienna, Austria). *Mikrochim. Acta*, 1956, (7-8), 1283-1309.—Following an introductory

review of geochemical data on concentrations of U in sea water and sea-bed layers, together with previously published methods for the determination of traces of U, a method is described for the separation of small amounts of U from trivalent Fe, Th, rare earths, Pb, Ca, Mg, Al and Cr which, after a preliminary ether extraction from HNO_3 soln., may accompany the U into the extract. The acetate complex of the U is prepared in the pH range of 4.25 to 5.25, and the soln. is passed through a column of the strongly basic ion-exchange resin Amberlite IRA-400 (acetate form). Under these conditions the negatively charged ions of U are absorbed by the resin, whilst positively charged acetate complexes of the other elements pass through the column. Two column operations are involved. The first permits the separation of up to 43 μg of U from other elements. The second somewhat modified design of column results in the removal of the last traces of Fe, Th, etc., from a maximum of 10 μg of U. An improved form of the Harris and Kolthoff polarographic method (*J. Amer. Chem. Soc.*, 1945, **67**, 1484, and 1946, **68**, 1175) for the final determination of the U in the pure eluate is described. This involves the catalytic nitrate wave, the supporting electrolyte being 0.01 N HNO_3 . The accuracy of the polarographic determination over the concentration range 0.01 to 1.0 μg per ml is within $\pm 5\%$. The analysis time is < 5 hr., compared with approx. 1½ days for the older procedure with double ether extraction followed by a fluorimetric determination.

D. F. PHILLIPS

100. Fluorescent X-ray spectrographic determination of uranium in waters and brines. W. L. Kehl and R. G. Russell (Gulf Res. and Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1350-1351.—The uranium is pptd. from the sample as its phosphate, with aluminium as a carrier, and the ppt. is ashed. The ash is irradiated in the most intense part of the beam from a molybdenum-target X-ray tube and the spectrum is recorded by a Norelco X-ray spectrograph, with a lithium fluoride analysing crystal. When the matrix contains no absorbing elements, 0.01 mg of U can be detected. With field samples, yttrium nitrate solution is added as an internal standard. Good recoveries were obtained on synthetic samples.

P. T. BEALE

101. The direct analysis of uranium-gallium alloys. G. W. C. Milner (Atomic Energy Res. Estab., Harwell, Berks., England). *Analyst*, 1956, **81**, 367-369.—In the method described, the Ga forms a complex with EDTA (disodium salt) soln. at pH 2 and the excess of EDTA is determined by back-titration with standard Fe^{3+} soln., with potassium benzohydroxamate as indicator. Interference by uranyl ions in the visual detection of the end-point is overcome by following the titration absorptiometrically. Uranium is first reduced to the quadrivalent state by passing the soln. through a lead reductor and is then determined volumetrically by titration with a standard ceric soln., with ferroin as indicator. Alloy samples are best dissolved in HNO_3 , but this must be removed by fuming with H_2SO_4 before application of the reductor. Interference by Ga is small. The determination of U should be made first so that the content of Ga is then known by difference, and the calculated amount of EDTA can be added in its determination.

A. O. JONES

102. Colorimetric determination of a small amount of fluorine with zirconium "phenylfluorone" complex. Hirotsoshi Sano (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1956, **5** (5), 283-290.—The Zr-"phenylfluorone" (2:3:7-trihydroxy-9-phenylfluorone) complex reacts with F^- in < 0.1 N HCl to give free "phenylfluorone." The amount of F is determined from the difference in extinction of the Zr-"phenylfluorone" soln. in the presence and absence of F^- at 540 m μ . The insol. complex is satisfactorily dispersed by the addition of ethanol and cyclohexanol. An HCl soln. of Zr (≈ 25 μg , 1 ml) is mixed with the sample soln. in a measuring flask (50 ml) and treated with HCl to produce a 0.05 N soln. An ethanolic soln. of "phenylfluorone" (30 mg in 150 ml of ethanol containing 1 ml of N HCl) (20 ml) and cyclohexanol (5 ml) are added and the extinction is measured. The presence of Ti, Th, Sn, Ge, Fe^{III} , Sb, As, Al, PO_4^{3-} and oxalate causes interference; F should be separated by distillation.

K. SAITO

103. Physical methods for registering measurements of small amounts of chlorine in gases. D. Enders (VEB Chem. Werke Buna, Schkopau). *Chem. Tech., Berlin*, 1956, **8** (2), 67-71.—Full descriptions are given of two automatic recording analysers for the continuous estimation of small quantities of free Cl in gas streams. One is for the higher ranges (up to 0.3% by vol. of Cl) and is particularly suitable for estimating the free chlorine content of HCl produced by the reaction between H and Cl. It is based on measuring the u.v. absorption of the Cl by a photo-electric cell, but a vacuum photo-electric cell (a caesium cell) is used instead of the usual selenium cell to obviate corrosion and to obtain more reliable results. The other, more sensitive, apparatus is for estimating much lower amounts (traces) of free Cl (0 to 0.001% by vol.) and is particularly useful for showing the free chlorine content of acetylene purified from compounds of S and P by treatment with chlorine water. In this apparatus the gas stream to be analysed passes through a wash-tower down which a stream of methyl red solution flows, thereby decolorising the soln. in proportion to the Cl contained in the gas. The degree of coloration is determined photo-electrically by passing the stream of soln. in front of illuminated vacuum photo-electric cells before and after passage through the wash-tower.

H. L. WHITEHEAD

104. Detection of chloride, bromide, iodide and thiocyanate. H. Weisz (Univ. Birmingham, England). *Mikrochim. Acta*, 1956, (7-8), 1225-1229.—Four known reactions have been modified so that each is specific for one ion in the presence of the other three ions. Three of the reactions (for I^- , Br^- and SCN^-) are conducted on spot-test paper; I^- are detected with starch after oxidation over HNO_3 ; Br^- by means of fluorescein following oxidation with H_2O_2 (the I^- are probably oxidised to IO_3^-); SCN^- by means of FeCl_3 - FeSO_4 soln. (1 g of each in 100 ml of H_2O plus 1 drop of HCl), which reduces interference from I^- to a minimum. The detection of Cl^- is by spot testing on a watch-glass with AgNO_3 after complexing I^- , Br^- and SCN^- with 8-hydroxyquinoline and H_2O_2 . The halogen ions are liberated from their silver salts by reduction with Zn in acetic acid.

D. F. PHILLIPS

105. A rapid method for the determination of bromide and of bromide and iodide separately in the presence of chloride. J. Bitskei (Tech. Univ.,

Budapest, Hungary). *Z. anal. Chem.*, 1956, **151** (6), 423-426.—The quant. oxidation of Br^- by ClO^- at pH 10 to 11 giving BrO^- is used for the rapid quant. determination of Br^- . The method developed differs from that for I^- (*Anal. Abstr.*, 1956, **3**, 2727) only in that the BrO^- present must be destroyed (by sodium phenoxide) before back-titration of the excess of ClO^- with $\text{Na}_2\text{S}_2\text{O}_3$. To determine Br^- and I^- separately in the presence of Cl^- , the sum of Br^- and I^- is determined first (by the method for Br^-), and I^- alone are determined subsequently in a second sample. J. P. STERN

106. Analytical separation of iodide and chloride with their cuprous salts. II. Determination of iodine by weighing cuprous iodide. Hisao Fukamauchi, Sachiko Obata and Kazuko Iiyoshi (Women's Dept., Coll. of Pharm., Ueno-sakuragicho, Taito-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (9), 1070-1073.—Since CuI is practically insol. in 0.1 N H_2SO_4 , the pptn. of CuI with CuSO_4 can be utilised for the gravimetric determination of I^- in a dil. Na_2SO_3 soln. in the presence of Cl^- (Fukamauchi *et al.*, *Ibid.*, 1954, **74**, 1014). The ppt. is successively washed with water, acetone and ether and dried at 110° . Iodate is reduced to iodide in an H_2SO_4 soln. containing Na_2SO_3 , and similarly determined. The average deviation from the calculated value is $< 0.5\%$ (relative). K. SAITO

107. Flame-photometric determination of manganese in vegetable ash in the presence of potassium and gallium. H. Kick (Agric.-chem. Inst., Univ. Bonn, Germany). *Z. anal. Chem.*, 1956, **151** (6), 406-413.—Manganese in a HCl or HNO_3 soln. of vegetable ash is determined flame-photometrically by the use of the triplet at 4030.8, 4033.1 and 4034.9 Å. Interference by K (lines at 4044.4 and 4047.4 Å) and by Ga (4033 Å) is practically additive and can thus be readily corrected. J. P. STERN

108. A new method for rapid determination of manganese and barium by spectrographic analysis. Tomio Okada, Shigeo Nakai and Tsunehide Kohzuma (Central Res. Lab., Maruzen Oil Co., Shimotsu, Wakayama). *Japan Analyst*, 1956, **5** (4), 203-205.—The rapid determination of Mn in steel and Ba (Ba naphthenate) in oil was studied by the use of a two-step filter and a standard sample, which contains exactly 1.0% of the element concerned. The log. of the concn. of the elements is calculated from an empirical equation under given conditions of exposure (condensed spark with Feussner's generator). This method minimises the time taken for analysis and enables a determination to be made with a relative error of $< 4\%$ for Mn and $< 9\%$ for Ba. K. SAITO

109. Analytical chemistry of rhenium. XXIII. Colorimetric determination of rhenium with 2:4-diphenylthiosemicarbazide. W. Geilmann and R. Neeb (Univ. Mainz, Germany). *Z. anal. Chem.*, 1956, **151** (6), 401-406.—Perrhenates give a characteristic red colour (λ_{max} 510 m μ) of high sensitivity with 2:4-diphenylthiosemicarbazide (I). The complex is extracted by CHCl_3 and is suitable for colorimetry. The method of preparing I is detailed. *Procedure*—Acidify the soln. of perrhenate (5 to 10 ml containing ≥ 50 μg of Re) with HCl until it is 6 N. Add the soln. (1.5 to 2.0 ml) of reagent (a soln. of I in methanol saturated at room temp.) and heat at $80^\circ \pm 2^\circ$ for 20 min. Cool rapidly under the tap and extract with CHCl_3 (25 ml). Compare the extinction of the organic phase at

510 m μ with a calibration curve. Results are not affected by the presence of alkali-metal chlorides; small amounts of molybdate (≥ 50 μg) cause slightly high results as molybdates also give a red colour with I. The accuracy for 3 to 50 μg of Re as perrhenate is generally within $\pm 0.5\%$.

J. P. STERN

110. Nitrosoresorcinol monomethyl ether [3-methoxy-5-nitrosophenol] as a reagent for iron and cobalt. S. M. Peach (Rugby College of Technol. and Arts, Eastlands, Rugby, England). *Analyst*, 1956, **81**, 371-373.—The preparation of the reagent from *m*-methoxyphenol is described. Ferrous iron produces a water-soluble green complex, soluble also in isoamyl and *n*-butyl alcohols. With Co a red-brown complex insoluble in water but soluble in various alcohols and in benzene is formed. Both complexes are detectable at high dilutions. For the determination of Fe^{2+} , a soln. of the reagent in glacial acetic acid or acetone is added to the suitably diluted soln. of Fe. The colour is measured absorptometrically, the max. extinction being between 700 and 710 m μ at an optimum pH of 2.0. Ferric iron does not interfere for 10 min., when its reduction by the reagent may set in. Within certain stated limits Ni and Cu do not interfere. In the presence of Co the colour due to Fe may be destroyed by addition of HCl and the residual absorption due to Co measured and deducted from the total absorption. With Co the complex is formed at pH 6 to 8 and has max. absorption at 380 m μ ; for measurement it is extracted with benzene. Ferric iron may also be determined after reduction of the sample soln. with SO_2 and removal of most of the gas. A. O. JONES

111. A conductimetric method for determining ferric iron. G. B. Pasovskaya. *Izv. Akad. Nauk, Turkm. SSR*, 1955, (2), 54-57; *Ref. Zhur.*, *Khim.*, 1955, Abstr. No. 52,179.—The method is based on the difference in electrical conductivity between a soln. of Fe^{3+} and of a soln. of the complex of Fe^{3+} with Na sulphosalicylate. To a definite vol. of sample, add sufficient 2 N HCl so that, after dilution to 20 ml, the pH will be 2.5 to 4.4, with the concn. of $\text{Fe}^{3+} \leq 0.0865$ g per litre. Titration is carried out with almost saturated Na sulphosalicylate, which has been standardised with a standard soln. of Fe^{3+} . The error is $\geq 0.5\%$.

C. D. KOPKIN

112. Absorption spectrophotometric analysis of complex sulphate of iron in the presence of molybdenum and vanadium. Masayoshi Ishibashi, Tsunenobu Shigematsu, Yuroku Yamamoto, Masayuki Tabushi and Toyokichi Kitagawa (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1956, **5** (5), 279-282.—The light absorption of Mo^{VI} and V^{V} in H_2SO_4 changes with concn. of H_2SO_4 . The addition of Na_2SO_4 (≈ 0.5 M) markedly increases the extinction coeff. of Fe (< 20 p.p.m.) at 300 m μ in 2 N HClO_4 , but not that of Mo or V. By measuring the extinction coeff. of the mixed soln. in 3 N HClO_4 and in 2 N HClO_4 containing 0.5 M Na_2SO_4 , Fe (1 to 15 p.p.m.) is determined in the presence of < 30 p.p.m. of V or < 50 p.p.m. of Mo. This method can be applied to the analysis of Fe-Mo or Fe-V alloys with a slightly greater error. K. SAITO

113. Volumetric analysis by the use of mercurous salt as reducing agent. Determination of ferric and cupric ions. Tsutomu Matsuo (Fac. of Liberal

Arts, Yamagata Univ., Koshirakawa-cho, Yamagata). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (12), 962-965.—Belcher's volumetric determination of Fe^{3+} and Cu with $\text{Hg}(\text{NO}_3)_2$ (*Anal. Chim. Acta*, 1951, **5**, 260; 1952, **7**, 470) was studied with reference to the equilibrium const. of the redox reaction. The determination of Fe (1 to 10 mg) is satisfactorily effected in 0.2 to 0.4 N HNO_3 in the presence of SCN^- (0.02 to 0.002 times the molar concn. of the Fe). Interference is caused by Cu, Co and > 25 mg of F^- , pyrophosphate and tartrate. Copper (> 10 mg) is similarly determined in the presence of SCN^- , with benzidine or o-dianisidine as indicator. K. SAITO

114. Colorimetric determination of trace amounts of antimony in steel. N. Leontovitch (Inst. Recherches de la Sidérurgie, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1956, **38** (8), 284-288.—Less than 0.01% of Sb in steel can be determined with high accuracy by measuring the extinction at $425 \text{ m}\mu$ of the coloured complex HSbI_4 formed in H_2SO_4 soln. by addition of an aq. soln of KI and ascorbic acid. Variables affecting the procedure are discussed. After acid dissolution of the sample (2 g), the metals are pptd. with H_2S in the presence of 50% tartaric acid (to sequester W and V) and Cd acetate (as carrier for Sb). The separation of Sb from Cd, Cu, Pb, etc., is made by digestion of the ppt. with aq. 10% sodium sulphide soln. at 60° to 70° for 2 hr. To prevent entrainment of Sb^{3+} in S, the sulphides in the filtrate of sulpho-salts are oxidised with boiling H_2O_2 before the acidification with tartaric acid to precipitate SiO_2 . The final clear soln., containing 20 ml of 20% (v/v) H_2SO_4 and 10 ml of KI-ascorbic acid reagent, is made up to 50 ml and the extinction is measured in a 5-cm cell, a blank being run at the same time. The colour develops quickly and is stable for 24 hr.; Beer's law is valid for 0.8 to $50 \mu\text{g}$ of Sb per ml. The method is applicable whatever the content of Mn, Cr, V or W, and for the usual concn. ($\approx 0.2\%$) of As or Sn, but a correction is necessary if $> 0.5\%$ of Mo is present. Selenium and Te interfere very seriously. W. J. BAKER

115. The photometric determination of silicon in steels. T. R. Andrew and C. H. R. Gentry (Philips Electrical Ltd., New Road, Mitcham Junction, Surrey, England). *Analyst*, 1956, **81**, 339-348.—An improved method based on the molybdenum-blue reaction is proposed for the determination of Si in steels. The sample is dissolved in 5% H_2SO_4 (for plain carbon and low-alloy steels) or in HNO_3 or mixed acid (for high-alloy steels) and, in the absence of HNO_3 , the soln. is oxidised with KMnO_4 , excess being removed with H_2O_2 . An aliquot portion of the diluted soln. is treated in this order with an ammonium molybdate soln. (I), an oxalic acid soln. (II) and a ferrous ammonium sulphate soln. (III). An equal aliquot is treated with the same soln. in the order II, I, III to provide the compensating soln. The extinctions of the two soln. are measured against water in the Spekker absorptiometer with an Ilford No. 608 filter or spectrophotometrically at $665 \text{ m}\mu$ for normal-range materials (up to 3% of Si with a 0.5-cm cell) or at $810 \text{ m}\mu$ for low-range materials (0.13% of Si with a 4-cm cell). The percentage of Si is ascertained from a calibration graph. A. O. JONES

116. Absorption-titration flask for determination of sulphur in steel. M. Roth and S. Lader (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1956,

28 (8), 1359.—An easily constructed, three-necked glass flask for use in the combined method of determining S and C in steel (*cf. Anal. Abstr.*, 1955, **2**, 579) is described and illustrated. A bubbling tube diffuses the combustion gases (CO_2 and SO_2) throughout the HCl soln., the iodate titration of the absorbed SO_2 being made during the absorption by inserting the tip of the burette into the flask.

W. J. BAKER

117. Determination of magnesium in nodular cast iron by spectrographic analysis. B. C. Kar and M. K. Gupta (Nat. Metall. Lab., Jamshedpur, India). *J. Sci. Ind. Res., B, India*, 1955, **14** (11), 570-572.—Small amounts of Mg in nodular cast iron are determined by a spectrochemical method by the use of standard metal electrodes. The standard and unknown samples are prepared in the form of rods, 3 to 4 cm long and 8 mm in diam. The upper electrode is a Johnson Matthey carbon rod, with a conical (80° angle) tip; the lower electrode is the sample, with a flat top. Spark excitation is carried out with secondary voltage 12,000 V, capacity $0.005 \mu\text{F}$, and spark gap 2 mm. A Hilger E 498 spectrograph, with slit width 0.015 mm , is used. A Hilger non-recording microphotometer, with slit width 0.15 mm , is used to measure the density of the spectral lines; the lines used are Mg 2802.7 Å and Fe 2783.69 (mainly), 2793.9 and 2779.3 Å. Comparisons with Gillam's method (*Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 499) are given; the greatest deviation is 23.7% in a sample containing 0.173% of Mg. I. JONES

118. Quantitative chromatography on treated paper. IV. Determination of the ferrocyanide ion by the measurement of the area of its chromatogram. Akira Murata (Dept. of Eng. Chem., Faculty of Eng., Shizuoka Univ., Oiwa-ke, Hamamatsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (4), 631-636.—The chromatographic determination of $\text{Fe}(\text{CN})_6^{4-}$ (10 to $500 \mu\text{g}$ in 0.1 ml) was studied on filter-paper impregnated with alumina (*cf. Anal. Abstr.*, 1955, **2**, 1443; 1956, **3**, 329). The sensitivity of the paper is adjusted by changing the concn. of HClO_4 with which the sodium aluminate is hydrolysed. An aq. soln. of $\text{Fe}(\text{CN})_6^{4-}$, containing SO_4^{2-} , SCN^- , acetate, Cl^- or Br^- , is adjusted to a pH of 5.5 to 9.5, then applied to the impregnated paper, developed with water and revealed with Fe^{3+} . The ease with which the absorption of the ion takes place decreases in the order given, whilst the R_F value increases in the same order. The spot of $\text{Fe}(\text{CN})_6^{4-}$ always occupies the lower part of the paper, the area being proportional to the amount present. Separation of the spots of PO_4^{3-} , F^- , oxalate or OH^- is unsatisfactory under the given conditions.

V. Micro-determination of the ferrocyanide ion by the measurement of the spectral reflectance of its chromatographic spot. Akira Murata. *Ibid.*, 1956, **77** (5), 781-786.—The amount of $\text{Fe}(\text{CN})_6^{4-}$ is evenly distributed in the spot obtained. When the cut-out spot is mounted for reflectance measurement, the overall reflectance bears a linear relationship to the amount of $\text{Fe}(\text{CN})_6^{4-}$ (0.5 to $10 \mu\text{g}$ per 0.05 ml) at $660 \text{ m}\mu$. Experimental conditions, including the pH (optimum 2.5 to 8.5), the time taken for adequate revealing of the colour (15 min.) and the amount of reagent used, were studied. The interference of other ions is almost the same as stated in Part IV, but the presence of SCN^- causes a decrease in reflectance [due to the red $\text{Fe}(\text{SCN})_6^{3-}$], resulting in too high values for $\text{Fe}(\text{CN})_6^{4-}$.

When the paper is treated with 0.01 *M* H_2SO_4 instead of HClO_4 the difference of the R_F values of these two anions is sufficient for a clean separation to be effected.
K. SAITO

119. General photometric micro-determination of cobalt with nitroso-R salt. W. H. Shipman and J. R. Lai (U.S. Naval Radiolog. Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1151-1152.—Cobalt can be determined photometrically with nitroso-R salt at 425 $\text{m}\mu$ if the excess of reagent is destroyed with KBrO_3 . The procedure described shows a fivefold increase in sensitivity over those methods in which 525 $\text{m}\mu$ is used. Methods are given for the determination of Co which include the removal of interfering ions and the approx. estimation of the concn. range, since Beer's law is obeyed only over the range 0.5 to 5 μg of Co per 5 ml of soln.
J. H. WATON

120. Development of a direct spectrophotometric micro-determination of cobalt on paper. A. Lacourt and P. Heyndrickx (Univ. Libre de Bruxelles, Belgium). *Mikrochim. Acta*, 1956, (9), 1389-1414.—The cobalt is determined by staining the paper with 1-nitroso-2-naphthol and measuring the extinction of the colour produced. The reproducibility of the method is within 1% for 0.1 to 3 μg .
C. A. SLATER

121. Composition of complex compounds of cobalt with dimethylglyoxime formed in the presence of sodium stannite. L. S. Nadezhina and P. N. Kovalenko (Rostov on Don State Univ.). *Zhur. Obshch. Khim.*, 1956, **26** (6), 1579-1585.—In the presence of Na_2SnO_3 and in alkaline or ammoniacal medium, Co reacts with 2 mol. of dimethylglyoxime (H_2Dm). In ammoniacal medium the compound $\text{Co}(\text{HDM})_2 \cdot 2\text{NH}_3$ is formed. The optimum conditions for the colorimetric determination of Co by means of the reaction are described. G. S. SMITH

122. Determination of small quantities of nickel with α -furildioxime. C. G. Taylor (U.K. Atomic Energy Authority, Windscale Works, Sellafield, Calderbridge, Cumberland, England). *Analyst*, 1956, **81**, 369-371.—In the method described, the slightly acid sample soln. containing up to 20 μg of Ni is treated with specified amounts of $\text{K}_2\text{Cr}_2\text{O}_7$, sodium citrate (to oxidise Fe and prevent pptn. of hydrolysable cations) and with α -furildioxime soln. (1% in 50% aq. ethanol) and aq. NH_3 . The red soln. is extracted thoroughly with chloroform and the extinction of the intensely yellow chloroform extract is measured in a Spekker absorptiometer with Ilford No. 601 filters against a reagent blank. The calibration graph is constructed with standard soln. of Ni by the same procedure. The absorption spectrum of the chloroform extract has a max. at 435 $\text{m}\mu$.
A. O. JONES

123. A rapid determination of a small amount of nickel by means of a detector tube. Yoshitaka Kobayashi (Fac. of Eng., Yokohama Univ., Minamiku, Yokohama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (10), 728-732.—A detector tube was devised for a rapid (< 15 min.) determination of Ni (0.01 to 3.0 mg per ml). Silica gel (60 to 80 mesh) (100 g) is mixed with an ethanolic soln. of dimethylglyoxime (1%, 100 ml) and gently dried. The treated silica gel (0.9 g) is placed in a glass tube (diam. 4.5 mm, length 20 cm). The sample soln. (pH 3 to 7, 1 ml) is passed through the tube and the length of the pink layer is measured. The concn.

of Ni is calculated from an empirical table. Interference is caused by Fe^{II} , Cu, Co, V, Pd and Pt. Results are in good agreement with those obtained by the gravimetric method.
K. SAITO

124. Determination of nickel, cobalt, chromium and manganese by flame photometry. F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asuncion Omarmenteria (Anal. Chem. Inst., Sci. Fac., Madrid, Spain). *An. Real Soc. Españ. Fis. Quím.*, B, 1956, **52** (4), 221-236.—The experimental conditions for the flame-photometric determination of Ni, Co, Cr and Mn are studied. The systems of interference which may occur in binary mixtures of either two elements in soln. together, or of one element in soln. with iron, are investigated. Some details of the problem of interference in soln. containing three elements are given. A collection of interference curves is included, and practical details for the determination of the elements, and for the correction of experimental values, are given. The method is used for the determination of the four elements in steel samples. An accuracy of $\pm 1\%$ is attained.
C. A. FINCH

125. The analysis of metallic nickel. VII. Determination of manganese. Shigeru Yokosuka (Bess Mine Office, Sumitomo Metal Mining Co. Ltd., Niihama, Ehime Prefecture). *Japan Analyst*, 1956, **5** (5), 282-285.—Manganese (< 0.01%) in Ni is co-pptd. with $\text{Fe}(\text{OH})_3$ in the presence of a large amount of NH_3 . No significant interference results from the presence of Pb (< 0.5 mg), As (< 0.02 g), Sb (< 0.5 mg) and Ni. *Procedure*—The sample (10 g) is dissolved in HNO_3 (1 + 1, 80 ml), and aq. NH_3 soln. (a 60-ml excess after neutralisation) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (5 g) are added. Iron alum soln. (1 mg of Fe per ml, free from Mn, 10 ml) is added and the pptd. $\text{Fe}(\text{OH})_3$ is filtered off, dissolved and similarly re-pptd. The ppt. is dissolved in HNO_3 (1 + 3, 100 ml containing 10 ml of 30% H_2O_2), heated and successively treated with 2 *N* H_2SO_4 (3 ml), 85% H_3PO_4 (5 ml), 1% AgNO_3 (2 ml) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (5 g). The resulting KMnO_4 is submitted to spectrophotometry at 530 $\text{m}\mu$.

VIII. Determination of silicon. Shigeru Yokosuka. *Ibid.*, 1956, **5** (5), 285-288.—Silicon (> 0.0002%) in Ni is converted into heteropoly-molybdate by the usual method and extracted from an acid soln. (> 0.9 *N*) with amyl alcohol. The molybdosilicic acid is transferred to an aq. layer of pH 11, containing 0.1 *N* NaOH and 4% H_3BO_3 , and submitted to photometry at 430 $\text{m}\mu$. No significant interference results from impurities, including As (< 0.5 mg) and Cr (< 0.2 mg). *Procedure*—The sample (10 g) is dissolved in 7 *N* HNO_3 (80 ml), treated with 3% H_2O_2 (1 ml), boiled and made up to 100 ml. A 10-ml portion is heated on a water bath for 5 min., diluted with water (30 ml) and treated with ammonium molybdate (10%, 2 ml) for another 10 min. The product is shaken with amyl alcohol (10 ml) and the organic layer is treated as described above.
K. SAITO

126. Fire assay for platinum. I. Hoffman and F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Anal. Chem.*, 1956, **28** (7), 1188-1193.—Acceptable recoveries of Pt are obtained by fire assay with a wide range of fluxes, nearly complete recovery being obtained with only one re-assay, except with acid fluxes of high SiO_2 content. Although losses during cupellation are insignificant, a loss of Pt occurs in some cases by migration to the pot wall. The presence of a high proportion of Ni in the ore

causes loss of Pt to the slag. A serious loss of Pt to the parting acid occurs in the presence of Cu and Ni. J. H. WATON

127. The use of ascorbic acid for the volumetric determination of platinum. E. A. Maksimuk. *Izv. Sektora Platin, I.O.N.Kh., Akad. Nauk SSSR*, 1955, (30), 180-182; *Ref. Zhur., Khim.*, 1955, Abstr. No. 52,190.—The method for the volumetric potentiometric determination of Pt^{IV} is based on reduction of K_2PtCl_6 with an excess of ascorbic acid, which is then titrated with 0.1 N $FeCl_3$ soln. The sample of K_2PtCl_6 is dissolved in 0.02 N HCl (pH 1.7) by warming on a water bath and cooling to room temp. A weighed quantity of ascorbic acid is dissolved at room temp. in 0.02 N HCl, and the two soln. are mixed. During the rapid reduction of the K_2PtCl_6 , the temp. must not be allowed to rise. The $FeCl_3$ soln. is standardised gravimetrically as Fe_2O_3 . C. D. KOPKIN

128. Determination of platinum and palladium in ferronickel assay buttons. H. G. Coburn, F. E. Beamish and C. L. Lewis (Univ. of Toronto, Ont., Canada). *Anal. Chem.*, 1956, **28** (8), 1297-1300.—A complete procedure for the determination of Pt and Pd in platinum ores, concentrates and ingots is described. The Pt and Pd are first collected from the crushed ore in ferro-alloy buttons at 1350° (2 to 15 min. reaction time). The buttons are digested in hot aqua regia for 12 hr., the soln. is evaporated to small vol. (i.r. lamp) to remove excess of acid and is then diluted to ≈ 1.5 litres with H_2O to a pH of 1.3 ± 0.2 . Iron, Ni and Cu are removed from this soln. by passing it through a cation-exchange column (Dowex-50; 60 cm \times 4 cm) at a rate of 25 ml per min. The column is washed with 1 litre of H_2O ; soln. containing >30 g of base metals should be divided into two portions and each portion passed through a freshly prepared column. After evaporation of the eluate, conversion of Pt and Pd into complex nitrites and removal (by double pptn. at pH 8) of trace amounts of unabsorbed base metals, the nitrite complexes are decomposed completely (conc. HCl) and the Pt and Pd are finally separated and determined by standard gravimetric and colorimetric methods. W. J. BAKER

129. The use of organic reagents (oximes) in the analysis of the platinum metals. N. K. Pshenitsyn and G. A. Nekrasova. *Izv. Sektora Platin, I.O.N.Kh., Akad. Nauk SSSR*, 1955, (30), 126-141; *Ref. Zhur., Khim.*, 1955, Abstr. No. 55,377.—The possibility of using oximes for the analysis of the metals of the platinum group and for the determination and removal of Pd from the platinum metals, gold and base metals was studied, with salicylaldehyde (I), benzoin α -oxime (II), β -furfuraldoxime (III) and α -furfuraldoxime (IV). The experiments were carried out on standard soln. of Pd, Pt, Rh, Ir, Ru, Ni, Cu, Fe^{III} and Pb, containing ≈ 1 g of metal per litre. It is established that a 1% aq. or aq.-ethanolic soln. of I can quant. precipitate Pd at a concn. of HCl of $>1\%$ or of H_2SO_4 of $>5\%$ by wt. A quant. separation of Pd by I from Pt, Ru, Ir and Au is effected only in the presence of an oxidant. In the presence of Au and Pt, 1 ml of conc. HNO_3 is added to the soln., and in the presence of Ru or Ir, 0.5 ml of 30% H_2O_2 . Under certain conditions Pd may be separated from Ni, Fe^{III} and Pb. A 2% alcoholic soln. of II precipitates Pd quant. in a weakly acid medium (0.14% HCl). The sensitivity of the reaction of II with Pd is so high

that this reagent may be used for the micro-determination of Pd. A 10% alcoholic soln. of III rapidly precipitates Pd in high concn. from pure soln., whilst a 1% aq. soln. of III precipitates Pd from soln. containing Pt, Ir, Ru, Ni, Cu and Fe^{III} at an HCl concn. of 2%. In the presence of Rh, the Pd-furfuraldoxime compound is re-pptd. A 10% soln. of IV precipitates Pd quant. at an HCl concn. of $>0.5\%$; Pt is pptd. by this reagent in 98 to 99% amounts only on prolonged heating. The Pd was determined gravimetrically in all cases.

C. D. KOPKIN

130. Assay for platinum metals in ores and concentrates. I. Hoffman, A. D. Westland, C. L. Lewis and F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Anal. Chem.*, 1956, **28** (7), 1174-1177.—Several platinum ores and concentrates were analysed by direct fire-assay and by methods involving a previous leaching process. The beads of Ag-Pt so obtained were examined spectrographically. No advantage appeared to be gained by leaching before the fire assay. J. H. WATON

131. Separation of fission products by distillation method. I. Distillation of carrier-free ruthenium with potassium dichromate. Tomihisa Kambara (Sch. of Chem., Fac. of Educ., Shizuoka Univ., Oiwa-cho, Shizuoka). *Japan Analyst*, 1956, **5** (4), 222-224.—Hume's distillation method was modified by the use of $K_2Cr_2O_7$ instead of $KMnO_4$. The fission products are heated with conc. H_2SO_4 and $K_2Cr_2O_7$ and the vapour is collected in an ice-cooled flask. The end of distillation is more easily indicated by colour change than when $KMnO_4$ is used. K. SAITO

132. Spectrographic solution methods for slag analysis. S. Bergenfelt (Surahammers Bruks Ltd., Sweden). *Jernkontor. Ann.*, 1956, **140** (1), 75-80.—Two methods for obtaining soln. of slag and for their spectrographic analysis are given. In the first method, HCl is used to dissolve the slag, with Cu as spectrographic reference. *Procedure (i)*—Blend 0.2 g of finely powdered slag with 4 g of CuO. Dissolve the mixture in 10 ml of HCl (1:1), evaporate to dryness, dissolve the residue in HCl, and filter to remove SiO_2 . Make the filtrate up to 50 ml with HCl, transfer a portion of the soln. into a glass cup and analyse by means of an a.c. spark and a rotating graphite disc dipping into the soln. In the second method, Co is added as reference. *Procedure (ii)*—Melt 0.02 g of finely ground slag in a platinum crucible with 0.4 g of anhyd. $Na_2B_4O_7$. Dissolve the melt in 10 ml of citrate soln. [45 g of citric acid, 25 g of $Co(NO_3)_3$ and 400 ml of H_2O], heating to $<80^\circ$; transfer ≈ 3 ml to a glass cup and obtain the spectrographic reading as in the first method. H. A. FISHER

See also Abstracts 2, 3, 4, 8, 10, 16, 142, 192, 193, 194, 197, 320.

3.—ORGANIC ANALYSIS

133. The error in organic micro-analysis. I. Sources of error in determination of carbon and hydrogen. Hiroshi Fujiwara and Masami Kan (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-nishinocho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (10), 1213-1218.—Analytical data (>300 for each sample) for the determination of C and H in cane sugar, hippuric acid, acetanilide and cholesteryl benzoate were collected at random

and statistically analysed. The values show normal distribution and the precision is $\pm 0.25\%$, being in good agreement with the value (0.3%) normally approved. There appears to be a significant difference between values obtained by different analysts.

K. SAITO

134. Dry combustion and volumetric determination of isotopic carbon and hydrogen in organic compounds. Removal of nitrogen dioxide, and gas temperature correction factors. D. R. Christman, J. E. Stuber and A. A. Bothner-By (Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1345-1347.—Small amounts of NO_2 in the presence of excess of O will pass through a radiator trap cooled in "dry ice" at low pressures. In the method of Christman *et al.* (*Anal. Chem.*, 1955, **27**, 1935), involving the dry combustion of organic compounds, the inclusion of such a trap makes possible the freezing-out of water before removal of the NO_2 by a manganese dioxide trap. A temp. correction giving an empirical correction of greater magnitude than that calculated by the ideal gas law was also applied to give more consistent results. Carbon values, with this correction, showed an average deviation of 0.24% from the theoretical.

G. P. COOK

135. Methylmagnesium chloride as reagent for determination of reactive hydrogen. G. D. Stevens (Ansul Chemical Co., Marinette, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (7), 1184-1186.—Two improvements are suggested for the Zerewitinoff method for determining active H in organic compounds. Methylmagnesium chloride is substituted for the iodide, and tetraethylene glycol dimethyl ether is used as solvent instead of diisopentyl ether. The solvent has the advantage of a low v.p., and readily dissolves many of the compounds containing active H.

J. H. WATON

136. General colour reaction for nitrogen compounds. Ehrlich's reagent in toluene and ethyl alcohol. C. Menzie (Johns Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1321-1322.—Ehrlich's reagent in toluene and/or ethanol soln. produced a colour with every class of nitrogen compound tested. The colours obtained with ≈ 70 nitrogen compounds are listed.

G. P. COOK

137. A modified micro-Dumas method for rapid determination of nitrogen. G. D. Shah, V. S. Pansare and V. N. Mulay (Nat. Chem. Lab., Poona, India). *Mikrochim. Acta*, 1956, (7-8), 1140-1143 (in English).—The Pregl-Dumas nitrogen method has been modified so that three successive determinations of N may be completed in a total time of 60 to 90 min. without changing the temporary filling or discontinuing heating. This minimises the positive error due to air absorption by the copper oxide. The usual carbon and hydrogen combustion-tube of Niederl and Niederl is used with modified filling and analysis procedure.

D. F. PHILLIPS

138. The micro-analysis of fluorine-containing organic compounds. V. The determination of nitrogen. R. Belcher and A. M. G. Macdonald (Univ. Birmingham, England). *Mikrochim. Acta*, 1956, (7-8), 1111-1115 (in English).—The nitrogen method of Kirsten (*Mikrochem.*, 1952, **39**, 245, and 1953, **40**, 121) has been slightly modified for the determination of N in solid and non-volatile liq. fluorinated compounds. Boats made from nickel

gauze replace the original nickel-gauze capsules for the temporary filling. The combustion-tube life is considerably prolonged by (i) addition of granular silica to the temporary filling to reduce fluorine attack; (ii) by loose packing of the permanent filling; and (iii) by maintaining the furnace at working temp. when not in use. Conditions are given for successful decomposition of most types of fluorine-containing compounds and suggestions are made for dealing with even more refractory compounds. The average deviation from the theoretical for 25 successive analyses was 0.048% .

VI. The determination of sulphur. R. Belcher and A. M. G. Macdonald. *Ibid.*, 1956, (7-8), 1187-1192 (in English).—Decomposition of the organic compound is accomplished by fusion with sodium metal in a nickel bomb at 600° . The sulphide formed is oxidised to sulphate and then pptd. as BaSO_4 . After filtration on a pulp pad, the BaSO_4 ppt. is boiled, together with the pad, in a soln. of EDTA and aq. NH_3 . Excess of EDTA remaining after reaction with Ba is determined by back-titrating with $0.01 M \text{MgCl}_2$ soln., with Eriochrome black T as indicator. The addition of boric acid prevents co-pptn. of BaF_2 . The accuracy of the determination with 3 to 10 mg of sample is that of normal micro-procedures. The method is applicable to a wide range of compounds, including those containing phosphorus.

D. F. PHILLIPS

139. Application of potentiometric silver titration, with reference potentials, to elementary organic micro-analysis. I. Introduction. Chlorine, bromine and iodine. R. Levy (Lab. Municipal de Paris, 39 rue de Dantzig, Paris). *Bull. Soc. Chim. France*, 1956, (3), 497-507.—The micro-determination of halogens in organic compounds is carried out after reaction with NaO_2 , KNO_3 and sucrose in a micro-bomb. After neutralisation with H_2SO_4 , the resulting Cl^- , Br^- and I^- cannot be determined by direct titration with AgNO_3 owing to the interference of the high concn. of Na_2SO_4 in the resulting soln. The end-point of the titration can be determined by the accurate measurement of the apparent e.m.f. at the equivalence point in a special potentiometric cell having a silver electrode against a high-resistance S.C.E. For consistent results the details of the test must be closely followed. Chlorine is determined in a 5-mg sample with $0.01 N \text{AgNO}_3$, and Br is determined in a 2- or 3-mg sample with $0.002 N \text{AgNO}_3$; I is similarly determined, but the IO_3^- produced by the primary reaction is first reduced to I^- with hydrazine sulphate. The following limits of error are claimed— Cl , $\pm 0.2\%$; Br , $\pm 0.1\%$; and I , $\pm 0.1\%$.

II. Chlorine, bromine and iodine in binary and tertiary mixtures. R. Levy. *Ibid.*, 1956, (3), 507-517.—The method is applicable to the determination of Cl , Br and I in the presence of each other. The determination is carried out in stages and a suitable correction is applied to the results. The limits of error are of the same order as those for the determination of the individual elements.

III. Phosphorus and arsenic. R. Levy. *Ibid.*, 1956, (3), 517-527.—Phosphorus and As can be determined in organic compounds after Kjeldahl digestion of a 5-mg sample. The resulting acid liquor is neutralised with NaOH , an excess of $0.03 N \text{AgNO}_3$ soln. is added to the soln. of PO_4^{3-} or AsO_4^{3-} and the ppt. is removed by vacuum filtration through borax. The AgNO_3 in the filtrate is determined potentiometrically by back-titration with $0.03 N \text{KCl}$ by the method given in Part I. The limits of error are— P , $\pm 0.1\%$, and As , \pm

0.2%. The determination is not affected by the presence of halogens in the compound.

H. B. HEATH

140. The determination of metals in organic compounds. A. Sykes (Univ. Birmingham, England). *Mikrochim. Acta*, 1956, (7-8), 1155-1168 (in English).—This is a review of developments since 1951 in methods for the determination of metals in organic compounds. (58 references.)

D. F. PHILLIPS

141. Micro-determination of methyl groups attached to carbon. V. H. Tashinian and M. J. Baker (Univ. of Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1304-1308.—A study of the dichromate oxidation of aliphatic compounds containing methyl groups is presented. Samples were digested in sealed tubes in a rocking furnace. A jacketed distillation apparatus, used in the acetic acid distillation step, eliminated carry-over of H_2SO_4 spray and reduced the distillation time for substances boiling in the range 110° to 118° . Acetic acid is quant. produced from several low-boiling aliphatic compounds, but not from terminal methyl groups attached to aliphatic amines of low mol. wt.

G. P. COOK

142. A rapid turbidimetric determination of acetylene in liquid oxygen by the silver acetylene method. Ohiko Kamimori and Yasuo Baba (Yawata Plant, Yawata Seitetsu Co. Ltd., Yawata, Fukuoka Prefecture). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (7), 538-540.—A rapid turbidimetric method (< 1 hr.) for the determination of acetylene (I) in liquid oxygen (0.2 to 2.0 mg per 5 litres) was studied. The sample (100 ml of liquid O) is set aside in a test-tube until the vol. decreases to ≈ 20 ml. The tube is then placed in a vacuum flask and stoppered so that the gas flows through an absorber tube containing 100 ml of ammoniacal $AgNO_3$ soln. (4% aq. $AgNO_3$ soln. containing $\approx 3.5\%$ of aq. NH_3 soln.); air is passed in the sample container to remove the last traces of I. The absorbing soln. is kept on a boiling-water bath for 5 min., then cooled; and the extinction of the turbid soln. is measured at 500 $m\mu$. The extinction is proportional to concn. of I of 0.2 to 2.0 mg per 5 litres of sample. The results compare favourably with those obtained by the Illosvay gravimetric method (*Ber.*, 1899, **32**, 2697).

K. SAITO

143. A rapid method for the determination of ethylene oxide vapour in the atmosphere by means of a detector tube. Tetsuzo Kitagawa and Yoshitaka Kobayashi (Fac. of Eng., Yokohama Univ., Minami-ku, Yokohama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (7), 514-517.—A simple detector was devised for the rapid (< 3 min.) determination of ethylene oxide (I) (30 p.p.m. to 4%) in the atmosphere. Silica gel (40 to 60 mesh, 100 g) is mixed with H_2SO_4 (6%) (100 ml) containing 6% of $K_2Cr_2O_7$ and dried at $\approx 100^\circ$. The yellow-orange powder (≈ 0.2 g) is placed in a glass tube (diameter 2 mm, length 5 to 7 cm). The sample of air (100 ml) is passed through the tube (at 1 ml per sec.) and the length of the resulting dark-green layer is measured (limit of detection, 0.001%). The length of this layer is proportional to the concn. of I in the range 0.5 to 4%. Its concn. in air is calculated by the use of an empirical table (for the correction of the effect of temp.). For < 0.5% of I, sufficient air is passed through the tube to produce a green layer whose length corresponds to a concn. of 0.1%. The amount of the

sample is measured and the concn. is calculated from another empirical table. The detector can be used in the presence of vapours of water, NH_3 , acetylene and nitrobenzene. Alcohols, ethers, aldehydes, acetone, aniline, H_2S , SO_2 and CS_2 interfere.

K. SAITO

144. The quantitative determination of organic peroxides. I. Two colorimetric methods. K. Ueberreiter and G. Sorge (Fritz Haber Inst., Max Planck Ges., Berlin-Dahlem, Germany). *Angew. Chem.*, 1956, **68** (10), 352-354.—The two methods described have the advantage of using homogeneous organic solvents, which facilitates the determination of organic peroxides. In the first method the reagent consists of a 0.05% to 0.1% soln. of specially purified diaminodiphenylamine base in glacial acetic acid, which is further diluted with benzene. The indamine formed on oxidation has an intense blue colour, having max. extinction at 640 $m\mu$. The method is strongly influenced by pH. The reagent for the second method is a soln. of the leuco base of methylene blue; the equipment used for the preparation of the base under nitrogen is described in detail. A 1-ml aliquot of the reagent soln. is diluted with 10 ml of a 0.5% soln. of trichloroacetic acid in benzene, the peroxide soln. is added, and the vol. is made up to 20 ml with the trichloroacetic acid soln.; the max. extinction is at 645 $m\mu$. As little as 0.03 μg of active oxygen can be detected, at a limiting concn. of 1 in 3×10^7 .

II. Test of the methylene-blue method. G. Sorge and K. Ueberreiter. *Ibid.*, 1956, **68** (15), 486-491.—The action of some organic peroxides [fluorenone (I), 1:1'-dihydroxydicyclohexyl (II), 1-hydroxy-1'-hydroperoxydicyclohexyl (III), benzoyl (IV) and lauroyl (V) peroxides, *tert*-butyl hydroperoxide (VI), and di-*tert*-butyl peroxide (VII)] on leucomethylene blue (VIII) is examined. It is shown that I, II and III act rapidly on VIII, but the higher peroxides IV, V and VI act much more slowly. The blue colour produced (λ_{max} , 643 $m\mu$) has the same concn. - extinction curve irrespective of the constitution of the peroxide (for compounds I to VI, inclusive) and VIII is thus suitable for the determination of peroxides in general. *Procedure*—Add a soln. of VIII (0.3 g) in benzene (1 ml) to a 0.15 to 0.5% soln. (IX) (15 ml) of trichloroacetic acid in pure benzene; then add ≈ 2 ml of a 10^{-4} M soln. of the peroxide in benzene and dilute to 20 ml with the soln. IX. Read the extinction at 643 $m\mu$ after approx. 5 min. and compare it with that of a blank soln. The soln. of VIII ages slowly and its extinction must be ≈ 0.05 . Since VII does not react with VIII under these conditions, the method can be used for the analysis of mixtures of VI and VII.

H. A. FISHER

J. P. STERN

145. Densities, refractive indices and rotations of mixtures of active amyl and isoamyl alcohols. R. M. Ikeda, R. E. Kepner and A. D. Webb (Univ. Calif., Davis, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1335-1336.—The dependence of density, refractive index and observed rotation on composition for mixtures of active amyl (2-methyl-1-butanol) and isoamyl alcohols is presented. The departures from linearity in the density - composition and refractive index - composition functions support the conclusion that active amyl and isoamyl alcohols do not form ideal soln. on being mixed. Deviations from ideality are largest for mixtures containing > 70% of active amyl alcohol.

G. P. COOK

146. Paper-chromatographic separation of aldehydes by means of their reaction with benzenesulphohydroxamic acid. H. Struck (Max Planck Inst., Berlin-Dahlem). *Mikrochim. Acta*, 1956, (7-8), 1277-1282.—A new method of separating aliphatic, unsaturated and aromatic aldehydes and also furfuraldehyde is described. The aldehyde is treated with benzenesulphohydroxamic acid to form the corresponding hydroxamic acid and chromatographed for 18 hr. at room temp., by the ascending method. After drying in air, the paper is developed by spraying with FeCl_3 soln. (2% in H_2O). Detection limits are—formaldehyde 20 μg , acetaldehyde 50 μg , crotonaldehyde 80 μg , furfuraldehyde 50 μg , benzaldehyde 50 μg , salicylaldehyde 50 μg , cinnamaldehyde 100 μg and phthalaldehyde 50 μg . Formaldehyde may also be detected chromatographically in the form of hexamine by treatment with dilute aq. NH_3 soln. and running for 18 hr. on the paper at room temp. The developing soln. is butanol-aq. NH_3 soln. (0.880) - H_2O (4:1:5). After air-drying, the chromatogram is sprayed with 2 N acetic acid and dried for 10 min. at 80°. The liberated formaldehyde is then stained with aniline phthalate, when its presence is shown by a pale lemon-yellow spot. The limit of detection is 3 μg of formaldehyde. D. F. PHILLIPS

147. Determination of free formaldehyde in a reaction mixture of dicyandiamide and formaldehyde. Uichiro Miyaoka and Takeo Matsui (Fac. of Eng., Fukui Univ., Makishima-cho, Fukui). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (8), 567-571.—Formaldehyde (I) in a reaction mixture with dicyandiamide reacts with Na_2SO_3 in a phosphate buffer of pH 6.8 to give NaOH equiv. in amount to the I. The reaction product, hydroxymethyl dicyandiamide, fails to show a similar reaction at a pH of < 7.2. The reaction mixture (0.8 ml) [containing ≈ 0.25 N $\text{Ba}(\text{OH})_2$] is poured into a phosphate soln. (a mixture of $1/3$ M Na_2HPO_4 and 10 ml of 0.5 M Na_2SO_3 neutralised with 0.1 N NaOH , with 0.1% phenolphthalein and naphtholphthalein as indicator, and mixed with 25 ml of 0.1 N HCl) and set aside for 3 min. to complete the reaction with Na_2SO_3 . The soln. is back-titrated with 0.1 N NaOH . K. SAITO

148. Chromatographic separation of acetaldehyde from vinyl acetate, and details of a rapid method for its estimation. O. Frehden and T. Ecsichof. *Rev. Chim., Bucharest*, 1956, **7** (5), 304-308.—Acetaldehyde is removed from vinyl acetate on a column of $\text{Na}_2\text{S}_2\text{O}_5$, when it is held as the bisulphite compound. With repeated runs through the column, the acetaldehyde content can be reduced to < 0.1%. A rapid method of estimating acetaldehyde in vinyl acetate lies in the addition of a known excess of NaHSO_3 to a suitable vol. of the sample, followed by the back-titration of the unreacted NaHSO_3 with 0.1 N I soln. J. H. WATON

149. Spectrophotometric determination of acetone by the salicylaldehyde method. S. Bernstson (AB Pripp & Lyckholm, Gothenburg, Sweden). *Anal. Chem.*, 1956, **28** (8), 1337.—The colorimetric determination is much improved by using pure salicylaldehyde instead of an ethanolic soln. of salicylaldehyde. The results are in agreement with Beer's law and the colour is stable for several hours after the initial 2-hr. development. The relative error, in the range 0.00015 to 0.0028 millimole, was less

than 2%. The procedure can be applied to the determination of acetone in aq. soln.

G. P. COOK

150. Calculations on the countercurrent separation of weak acids and bases. H. Mitchner and L. M. Parks (Univ. Wisconsin, Sch. of Pharmacy, Madison, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 546-548.—The partitioning of weakly acidic or basic organic systems can be altered according to a simple linear relationship if the partitioned substances possess a linear partition isotherm (that is, behave ideally). This enables conditions (e.g., of pH) to be selected for the optimum separation of two such substances by countercurrent distribution. It is then possible to predict in a simple manner the number of transfers to give a desired separation and to calculate the purity that will be attained. A. R. ROGERS

151. Determination of carboxylic acids, acid chlorides, and anhydrides by chlorine-36. Isotope-dilution method. P. Sorensen (Sadolin & Holmblad Ltd., Copenhagen, Denmark). *Anal. Chem.*, 1956, **28** (8), 1318-1320.—The compound to be analysed is quant. converted into the *p*-chloroanilide. This is then determined by a normal isotope-dilution method in which the ^{36}Cl -labelled *p*-chloroanilide of the relevant acid is used. Recoveries of > 97% were obtained with acetic acid and its anhydride, and benzoic and stearic acids. G. P. COOK

152. Pharmaceutical studies on mesoxalic acid. I. Micro-determination of mesoxalic acid and related compounds. Eiji Ochiai, Toshihiko Okamoto and Tohru Ueda (Pharm. Inst., Med. Fac., Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (11), 1338-1341.—The paper-chromatographic separation and colorimetric determination of mesoxalic acid (I) and tartronic acid (II) were studied with biochemical samples. An aq. or ethanolic soln. of I (5 to 50 μg) is passed through a column of Amberlite IR-120 and converted into its *p*-nitrophenylhydrazone, which is submitted to paper chromatography by the use of a mixture of isoamyl alcohol, formic acid (90%) and water (40:8:10) (R_F 0.42). I is thus separated from other ketonic acids, including glyoxylic, α -oxoglutaric and pulvic. The spot is cut out, eluted and colorimetrically determined by Cavanilli's method in a basic soln. (*Nature*, 1949, **163**, 568; **164**, 792). II (< 10 μg) produces molybdenum blue on being treated with molybdophosphoric acid, and can be photometrically determined (max. absorption 660 $m\mu$) in the presence of I, malonic, oxalic, lactic, glyoxylic and trichloroacetic acids, and glucose. K. SAITO

153. Paper-chromatographic separation of aliphatic dicarboxylic acids. A. Seher. *Fette u. Seif.*, 1956, **58** (6), 401-403.—Efficient separation of the dibasic acids from oxalic to sebacic cannot be achieved when a mixture of the acids is chromatographed on S. & S. paper No. 2043b by the method of Long *et al.* (*J. Chem. Soc.*, 1951, 2197). With a mobile phase of aq. N NH_3 in 60% ethanol, the difference between the R_F values of oxalic and sebacic acids is 0.33; with 70% ethanol the difference is 0.45, with 75% 0.41, with 80% 0.34 and with 90% 0.21. All the acids can be satisfactorily separated on S. & S. No. 2040a paper with aq. N NH_3 in 78% ethanol as mobile phase; the R_F values range from 0.13 (oxalic acid) to 0.81 (sebacic acid). For identification, the paper is dried in air for 2 to 3 hr. and then sprayed with a soln. of 0.2% ninhydrin and 0.05% ascorbic acid in ethanol. The

sprayed paper is placed in an oven at 120° and the spots develop after 1 to 2 min. The method is useful for the identification of acids produced by ozonolysis or permanganate oxidation of unsaturated compounds. E. HAYES

154. The detection of dicarboxylic acids on paper chromatograms. K. Bina and J. Kalamar (Slovak. Tech. Hochschule, Bratislava). *Naturwissenschaften*, 1956, **43** (2), 36.—When chromatograms are heated at 150° to 160° for 15 min., the dicarboxylic acids appear as brown bands on the paper. The brown material shows a yellow fluorescence in u.v. light if the acids are present in fair concn. Lower concn. of the acids yield chromatograms that show a blue fluorescence. Citric acid can also be detected by this test, separation being by means of the solvent ethanol-5% aq. NaOH (9:1). E. KAWERAU

155. The identification of citric acid, aconitic acid and tartaric acid on paper chromatograms. K. Schreier and W. Hack (Univ. Kinderklinik, Heidelberg). *Naturwissenschaften*, 1956, **43** (8), 178-179.—Descending chromatography on Whatman No. 1 paper is recommended with a butanol-acetic acid-water (4:1:1) solvent mixture. After being dried at room temperature, the paper is sprayed with a reagent comprising a 4% solution of *p*-dimethylaminobenzaldehyde in acetic anhydride to which a few crystals of anhyd. Na acetate have been added. The paper is then put into the hot air oven at 140° for 1 to 2 min. Citric acid yields a deep-purple spot, aconitic acid a wine-red coloration and tartaric acid a reddish-orange coloration. The coloration with malonic acid is dark green. Other acids of the citric acid type give no colour with this reagent. The lower limit of sensitivity of the reagent for the three acids is approximately 1 µg. E. KAWERAU

156. Spot tests for detection of N-nitroso compounds (nitrosamines). F. Feigl and C. Costa Neto (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1956, **28** (8), 1311-1312.—N-Nitroso compounds can be hydrolysed to the corresponding NH compounds by a wet method under mild conditions and a dry method by heating with hydrated ZnSO₄ or MnSO₄. The nitrous acid which splits off can be detected by the colour reaction with Griess reagent or by pptn. with sulphamic acid and BaCl₂. The limits of detection for various nitrosamines were between 0.5 and 15 µg. G. P. COOK

157. The separation of α - and β -glycerophosphates by paper chromatography. W. Dierick, J. Stockx and L. Vandendriessche (Lab. Physiol. Chem., Ghent, Belgium). *Naturwissenschaften*, 1956, **43** (4), 82-83.—Over-run chromatograms on Whatman No. 1 paper are recommended. Preliminary treatment of the paper with EDTA (disodium salt) and 8-hydroxyquinoline is advisable and the tanks must be left 24 hr. for equilibration before commencing the run. β -Glycerophosphate is the faster running in any one of the four following solvent systems—(i) *n*-propanol-aq. NH₃-water (6:3:1), (ii) *n*-propanol-acetic acid-water (8:1:1), (iii) isopropyl alcohol-pyridine-water-ethyl acetate (2:1:1:2), and (iv) nitromethane-pyridine-water (5:6:4). System (iv) gave the best separations and gave satisfactory results even on untreated paper. E. KAWERAU

158. Separation of mercaptans [thiols] by gas-liquid partition chromatography. S. Sunner, K. J. Karrman and V. Sundén (Lund Univ., Sweden). *Mikrochim. Acta*, 1956, (7-8), 1144-1151 (in English).—The technique of James and Martin (*Biochem. J.*, 1952, **50**, 879; 1952, **52**, 238, 242) was used for the quant. separation of a number of aliphatic thiols on the ultra-micro scale. A column packed with carborundum (mesh 180 to 220) was used with dioctyl phthalate containing 5% diphenylamine as the liq. phase. Oxygen-free N was used as the carrier gas, the column being surrounded by a steam jacket. The effluent gas was passed into a soln. of I and KI in 70% ethanol constituting a redox half-element. Thiols were quant. absorbed and oxidised by the I soln., thus changing the ratio I⁻:I and hence the potential of the element, which was directly recorded. With a 2.4-m column, up to 200 µl of mixture could be analysed with an accuracy within ± 0.04 micro-equiv. Tertiary thiols are not quant. oxidised by the I, and although their presence affects results for normal thiols the error is not serious. D. F. PHILLIPS

159. Rapid determination of carbonyl content in acrylonitrile [vinyl cyanide]. R. L. Maute and M. L. Owens, jun. (Monsanto Chemical Co., Texas City, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1312-1314.—The acetaldehyde content of vinyl cyanide is found by allowing the sample to react with hydroxylamine hydrochloride in methanolic soln. for 1 min. before titration of the liberated acid with methanolic NaOH to the thymol blue end-point. Total carbonyls are determined by increasing the reaction time to 5 min. The precision for acetaldehyde is within $\pm 0.003\%$ over the range 0 to 0.1%, and for high-mol-wt. ketones or mixtures of carbonyls the precision is within $\pm 0.005\%$. G. P. COOK

160. Determination of methylene chloride [dichloromethane] in aqueous solutions. B. M. Templeman and J. Juneau (Canadian Celanese Ltd., Drummondville, P.Q., Canada). *Anal. Chem.*, 1956, **28** (8), 1324-1325.—The dichloromethane is saponified with NaOH in an apparatus resembling the Parr peroxide bomb which is used to overcome loss of dichloromethane during hydrolysis. The Cl⁻ are measured by titration with AgNO₃. Recoveries > 96% were obtained from synthetic samples containing 0.25 to 1.25% of dichloromethane; the relative mean deviation was $\pm 0.26\%$ and the relative mean error was $\pm 0.01\%$ at the 1.15% level. G. P. COOK

161. Studies on tannins. IV. Adsorption of tannic acid on formaldehyde-urea condensate and its application to the determination of tannic and gallic acids. Koiti Kimura, Sigeaki Kuwano and Hiroshi Hikino (Pharm. Fac., Univ. of Osaka, Hotarugaikae, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (8), 962-966.—The use of the white condensate prepared from urea (40 g in 500 ml of water), formaldehyde (40% aq. soln., 50 ml) and N HCl (5 ml) was studied for the separation of tannic acid (I) and gallic acid (II). The sample soln. (5 ml) containing both I and II (each < 5 mg) is treated with saturated NaCl soln. and the condensate (1.0 g), then filtered and washed a few times with saturated NaCl soln. The filtrate and washings are combined and made up to 25 ml; a 10-ml portion is treated with ammonium molybdate (1%, 2 ml) for the colorimetric determination of II. The sum of I and II is similarly determined in the initial soln. K. SAITO

162. Colorimetric determination of sugars with 3:4-dinitrobenzoic acid. Tsunematsu Takemoto, Koji Daigo and Tadao Takai (Pharm. Fac., Univ. of Osaka, Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (8), 1024.—An improvement on Borel's method (*Helv. Chim. Acta*, 1953, **36**, 801) is the extraction of the yellowish colour from an acidic soln. into isoamyl alcohol. The sample soln. (< 1 mg of sugar per ml) (1 ml) is mixed with 1 ml of 3:4-dinitrobenzoic acid (0.2% in 3-18% aq. Na_2CO_3 soln.) and kept in a boiling-water bath for 10 min. This soln. is cooled, made acid with conc. HCl (0.2 ml) and extracted with isoamyl alcohol (6 ml). The extinction of the organic layer at 395 μ is proportional to the concn. for pentoses, hexoses and some of their derivatives, the specific extinction coefficients being slightly different from one another. K. SAITO

163. Analysis of mixtures of D-glucose and D-mannose by paper electrophoresis. D. R. Briggs, E. F. Garner, R. Montgomery and F. Smith (Univ. Minn., St. Paul, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1333-1335.—Mixtures of D-glucose and D-mannose, in which there is a high ratio of the former to the latter, are separated by paper electrophoresis and the individual sugars are determined by the phenol- H_2SO_4 colorimetric method. The D-glucose moves more rapidly on the paper than does D-mannose. Recoveries of the sugars were > 97% for glucose-mannose ratios from 2.6:1 to 40:1, with Whatman No. 1 paper, 0.1 M borate buffer at pH 9.2, and at 600 V. A simple apparatus for the electrophoresis is described. G. P. COOK

164. Removal of silicates from solutions of sugars such as isomaltose and isomaltotriose. R. W. Jones, R. J. Dimler and C. S. Wise (U.S. Dept. Agric., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1352-1353.—Removal of silicates from soln. of sugars was effected by adding HF to the aq. soln. The resulting highly ionised fluorosilicic acid was then retained by an anion-exchange resin of low basic strength, such as Duolite A-4. Removal of other ionic material was achieved by use of a cation-exchange resin (Dowex 50). G. P. COOK

165. Determination of glucose, maltose and other fermentable oligosaccharides as well as of dextrans after addition of culture yeast. K. Täufel and K. Müller (Inst. für Ernährungsforschung in Potsdam-Rehbrücke, Germany). *Z. Lebensmittelforsch.*, 1956, **103** (4), 272-284.—A critical survey of the methods of biological determination and differentiation of saccharides is given. A short decomposition method is described, based on the work of Pan *et al.* (*Anal. Chem.*, 1953, **25**, 231), in which glucose can be fermented in 15 min., maltose in 2 hr., and other fermentable oligosaccharides (isomaltose, maltotriose and panose) within 6 hr. Starch hydrolysates, e.g., of starch syrup, are used and the constitutional linkages of four groups of substances (glucose, maltose, other fermentable oligosaccharides and dextrin) can be studied. The method gives results in good agreement with those of the standard fermentation method (48 hr.) and is suitable for the determination of dextrin. S. C. I. ABSTR.

166. Vanadimetric estimation of hydroquinone [quinol] and metol with diphenylbenzidine and N-phenylanthranilic acid as internal indicators. G. Gopala Rao and T. P. Sastri (Andhra Univ.,

Waltair, India). *Z. anal. Chem.*, 1956, **151** (6), 415-422 (in English).—Diphenylbenzidine (I) and N-phenylanthranilic acid (II) are used as internal indicators in the vanadimetric determination of quinol and metol. The reaction between these indicators and sodium vanadate is, however, retarded by the reaction products (benzoquinone and vanadyl salts), though accelerated by oxalic acid; this catalyst also counteracts the inhibition due to the reaction products. Thus titration of quinol and of metol with sodium vanadate, with I as internal indicator, is possible at room temp. in 2 N H_2SO_4 in the presence of sufficient oxalic acid; results agree closely with cerimetric results. The rapid reaction of II with vanadate is not completely restored under these conditions, and normal titration at room temp. is possible only in 4 N H_2SO_4 when II is used as internal indicator. *Procedure*—Add to the soln. of metol or of quinol in 2 N H_2SO_4 (for preservation), 10 N H_2SO_4 (5 ml) and N oxalic acid (3 ml) and dilute to 50 ml. Titrate with 0.05 N sodium vanadate, with I as indicator. J. P. STERN

167. Detection of aromatic aldehydes with tryptophan or peptone. Seiichi Okuma (National Hyg. Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (9), 1155-1156.—Aromatic aldehydes, their semicarbazones and thiosemicarbazones react with tryptophan or peptone (which contains tryptophan) in HCl to yield a violet, blue or green coloration. This reaction can be used for their detection on a micro scale ($\approx 5 \mu$). One drop of the sample soln. is treated with 10 to 20 mg of peptone and conc. HCl (0.5 ml) on a water bath for 1 to 2 min. Aliphatic aldehydes and some saccharides can react similarly. Amino acids other than tryptophan fail to bring about such a coloration. K. SAITO

168. Detection of hydroxybenzaldehydes and ureide compounds with dimethylglyoxime and thiosemicarbazide. Seiichi Okuma (Nat. Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (10), 1291-1292.—The development of a red to purple colour when dimethylglyoxime (I) reacts with thiosemicarbazide (II) or thiosemicarbazone in the presence of hydroxybenzaldehyde (III), its alkyl ether (IV) or ureide compounds (V) was used for the detection of III, IV or V in an HCl soln. An ethanolic soln. (one drop) of the sample is mixed with one drop each of an HCl soln. of I (0.3 g in 10 ml of HCl) and II (0.1 g in 3 ml of water and 7 ml of ethanol) and heated on a water bath (7 min.). The limit of detection is $\approx 10 \mu$ g for III and IV, and $\approx 5 \mu$ g for V. K. SAITO

169. Polarographic analysis of solutions of alkyl aryl ketones and benzaldehyde. R. H. Boyd and A. R. Amell (Lebanon Valley College, Annville, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1280-1282.—The polarographic characteristics of *tert*-butyl phenyl ketone, phenyl isopropyl ketone, phenyl *n*-propyl ketone and benzaldehyde, and mixtures of the ketones with benzaldehyde, are given. The half-wave potentials are independent of each other and are sufficiently separated so that mixtures can be analysed with errors of < 3% at concn. of $\approx 10^{-3}$ M. Diffusion currents are linear with concn. and are independent of the presence of other carbonyls. The most suitable solvent and electrolyte is 0.1 M LiOH in 50% aq. ethanol soln. G. P. COOK

170. Micro-determination of aromatic nitro compounds with sodium pentacyanoamminferroate. Seichi Okuma (Nat. Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (11), 1342-1345.—The detection of a micro amount ($\approx 1 \mu\text{g}$) of aromatic and heterocyclic nitro compounds was studied with sodium pentacyanoamminferroate (I), prepared from sodium nitroprusside and aq. NH_3 soln., and the possible reaction mechanism is discussed. One drop of the ethanolic soln. of the sample is mixed with one drop of 10% CaCl_2 or Na acetate and zinc dust (5 mg) and kept on a boiling-water bath for a few sec. A few drops of ethanol are added and one drop of a 1% aq. soln. of I is carefully poured down the wall of the vessel. Aromatic nitro compounds produce a violet, purple or green coloration on the boundary of the layers; nitropyridines give a violet coloration, nitropyrimidines an orange, green or purple coloration, whilst nitrofurans and aliphatic nitro compounds fail to give a coloration. K. SAITO

171. Determination of aromatic polynitro compounds and phenyl groups. Seichi Okuma (Nat. Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (11), 1430-1431.—*m*-Dinitrophenyl compounds yield a violet, blue or red coloration by a spot test of their ethanolic soln. with 2 N NaOH and acetone (limit of detection, $1 \mu\text{g}$). A similar colour reaction is brought about by only a few compounds, including *p*-nitrobenzaldehyde semicarbazone and *p*-nitrophenylhydrazine. *o*-Dinitrobenzene is detected by the use of its colour reaction with a reducing agent such as glucose in an ethanolic soln. containing 0.5 N NaOH. Some phenyl compounds are nitrated by heating with KNO_3 and concn. H_2SO_4 , extracted with CHCl_3 from an acid soln. and detected by either of these methods. K. SAITO

172. Chromatography of naphthalenesulphonic acids. G. Spencer and V. Nield (The Clayton Aniline Co. Ltd., Clayton, Manchester, England). *Chem. & Ind.*, 1956, (35), 922.—Naphthalene-mono-, -di- and -tri-sulphonic acids have been successfully separated by ascending paper chromatography. A conventional solvent (*tert*-butyl alcohol-*n*-butanol- H_2O 4:3:3) was used and the zones were located by means of a quartz-envelope u.v. lamp having its output in the 253-m μ region. O. M. WHITTON

173. Quantitative analysis by the use of infra-red spectra. V. Analysis of isomers of naphthalenesulphonic acid and those of β -naphtholsulphonic acid by the aluminium stearate method. Shigeyuki Tanaka (Inst. of Techno-anal. Chem., Faculty of Eng., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1956, **5** (4), 216-219.—Dolinsky's homogeneous dispersion method (*J. Ass. Off. Agric. Chem.*, 1951, **34**, 748) was applied to the i.r. spectrophotometric analysis of 1- and 2-naphthalenesulphonic acids (I and II) and three isomeric 2-naphtholsulphonic acids (III). A mixture of the isomers (250 mesh, 100 mg) is mixed with Al stearate (1% in CS_2) in a stoppered flask with small glass beads. The mixture is shaken (180 times per min.) for 2 hr. to produce an apparently homogeneous soln., which is submitted to i.r. spectroscopy. The average deviation for $< 3 \text{ mg}$ (per ml) of I and II is $\approx 1\%$ and that for $< 4 \text{ mg}$ of III is $\approx 2\%$, comparing favourably with the liquid paraffin and the potassium bromide tablet method.

VI. Detection and determination of a small amount of free organic acid by the use of solvent

effect. Shigeyuki Tanaka. *Ibid.*, 1956, **5** (5), 268-271.—Infra-red absorption of an organic acid due to its OH bond stretching vibration is observed at 3.4 to 3.8 μ in a non-polar solvent (e.g., CS_2) and at 3.0 μ in a polar solvent. A small amount ($> 0.04\%$) of acetic acid in alkyl acetates, benzoic acid in alkyl benzoates and methacrylic acid in methyl and ethyl methacrylate is easily detected by placing pure esters in the compensating optical path. The extinction coeff. is proportional to the concn. of the acid for $< 15 \text{ mg}$ per ml, with a standard deviation of $\pm 0.04\%$. This method can be extended to the detection of acid in acid anhydride and of monoesters in dicarboxylic acid di-esters, comparing favourably with the usual method in non-polar soln. K. SAITO

174. The quantitative determination of cyclohexanone in technical methylcyclohexanone by chromatographic separation on silica gel. J. Franc (Inst. Organ. Synthesis, Pardubice-Rybitvi, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (3), 581-585.—cycloHexanone (I) is separated from the three isomeric methylcyclohexanones and the dimethylcyclohexanones by partition chromatography on silica gel with cyclohexane (II) as solvent, and is determined colorimetrically as the 2:4-dinitrophenylhydrazone. Even 20% of cyclohexanol does not interfere, but the apparent content of I in II diminishes with time and must therefore be standardised. An accuracy within $\pm 4\%$ is attainable. A 65 to 75-cm column is used and the flow rate is 180 ml per hour. P. S. STROSS

175. A paper-chromatographic method for the detection of water in cyclohexanone and in cyclohexanol. A. Castiglioni (Inst. Market Res. of Turin Univ., Piazza Arbarello 8, Turin, Italy). *Z. anal. Chem.*, 1956, **151** (4), 269-270.—By this method, 3% of water in cyclohexanone and 5% in cyclohexanol can be detected. Place one drop of the sample on Whatman No. 1 paper, allow to evaporate for 2 min., and develop by ascending chromatography with a solvent comprising isobutyl alcohol (10 ml), acetone (2 ml), saturated Cu acetate soln. (4 drops) and glacial acetic acid (1 drop). Dry the paper at 100° and spray with a 0.2% soln. of rubenic acid in acetone. The presence of water is detected as a dark spot at the origin. P. S. STROSS

176. Analysis of pyridine and picoline fractions by use of infra-red absorption spectra. Tsugio Takeuchi and Shigeyuki Tanaka (Fac. of Eng., Yamanashi Univ., Motoyanagi-cho, Kofu). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (7), 505-508.—A binary mixture of pyridine (I) and α -picoline (II) can be analysed by the use of their i.r. absorption spectra (14.26 μ for I, 13.30 μ for II). The standard deviation measured by Youden's method (*Anal. Chem.*, 1947, **19**, 946) is $\approx \pm 1.5\%$ for 10 to 90% of I. Small amounts of II ($< 0.4\%$) in I and of I ($< 0.1\%$) in II can be determined by the use of the same bands. A tertiary mixture of β -picoline, γ -picoline and 2:6-lutidine can be analysed with the bands 14.14, 12.59 and 12.99 μ , respectively; the standard deviation for these results is ± 1.1 , 1.6 and 1.1%, respectively. K. SAITO

177. Spot-test procedures for differentiation of quinoline and isoquinoline. F. Feigl and V. Gentil (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1956, **28** (8), 1309-1310.—Oxidation with KMnO_4 in neutral or acid soln. converts quinoline

(I) into pyridine-2:3-dicarboxylic acid, which forms an insol. blue copper salt in weak mineral acid soln. No reaction is obtained with isoquinoline (II). I and II can be distinguished from each other by reduction with Zn and HCl. On subsequent oxidation, the dihydroquinoline yields a brown ppt. with $K_2S_2O_8$ and $CuSO_4$, or a red ppt. with bromine water. The dihydroisoquinoline gives no reaction with persulphate and only a slight coloration with bromine water. Quinaldine behaves like I, but is less sensitive. The limit of detection for I is 20 μg with $K_2S_2O_8$ reagent and 2.5 μg with bromine water.

G. P. COOK

178. Titration of salts as acids, and as bases, in non-aqueous media. C. Bergamini and G. Mattei (Anal. Chem. Inst., Univ., Florence, Italy). *Sperimentale*, 1956, 6 (1-3), 13-22.—The mono- and di-pirates of the dialkylaminoethyl and the dialkylacetamide derivatives of 4-mercaptopyridine are titrated as bases with $HClO_4$, in non-aqueous solvents, such as acetic acid, acetic anhydride, or an acetic anhydride-nitromethane mixture. The dialkylaminoalkyl derivative behaves as a di-acid base, and the dialkylacetamide derivative as a mono-acid base. The same compounds are titrated as acids with sodium methoxide in dimethylformamide. α -Methylisoxazole- γ -carboxylic acid is titrated as acid with sodium methoxide in a benzene-methanol (6:1) mixture. Changes in pH during titration are illustrated by curves.

C. A. FINCH

179. Microgram detection of 3-hydroxyflavones with aromatic diaryl borates. VI. Tetraphenyl diboroxide. R. Neu (Dr. Willmar Schwabe G.m.b.H., Karlsruhe, Germany). *Mikrochim. Acta*, 1956, (7-8), 1169-1174.—Tetraphenyl diboroxide reacts with 3-hydroxyflavones (I) to give intense bathochromism and fluorescence in u.v. light. By this means 0.1 μg of morin and 1 μg of quercetin can be detected. A 0.5% soln. of I in methanol is used. The detection limit for quercetin can be lowered to 0.5 μg by simultaneous addition of a long-chain quaternary ammonium compound, e.g., benzalkonium chloride (Zephrol). Colour and fluorescence indications are fully tabulated.

D. F. PHILLIPS

180. Chromothermographic analysis of gaseous hydrocarbons. R. Bucur ('Victor Babes' Univ., Cluj, Roumania). *Rev. Chim., Bucharest*, 1956, 7 (3), 163-165.—Components of a gaseous mixture are separated completely by a new chromatographic technique which combines development and thermal desorption. Round the column, which is packed with silica gel, is fitted an electric heater that provides a temp. gradient. The heater is moved downwards over the column during development. If the concn. of the eluted gases are measured by thermal conduction, the components of the gaseous mixture can be determined to within 2%.

J. H. WATON

181. Polarographic determination of elemental sulphur in liquefied petroleum gases. J. B. Gregory and G. Matsuyama (Union Oil Co. of Calif., Brea, Calif., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1343-1345.—Samples of liquefied petroleum gases, collected in specially fitted stainless-steel bombs, are allowed to volatilise. Elementary S remaining in the bomb is dissolved in a pyridine-methanol-HCl soln. and the S in the soln. is measured polarographically. For concn. of S < 1 p.p.m. the precision and accuracy are within 0.02 p.p.m.

G. P. COOK

182. Determination of unsaturated hydrocarbons by low-voltage mass-spectrometry. F. H. Field and S. H. Hastings (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1248-1255.—In the determination of unsaturated in petroleum naphthas, mass spectra were used in which all peaks but those due to the molecule ion or ions were eliminated by reducing the ionising voltage to a value between the ionising potential of the molecule and the lowest appearance potential. The ionising current, ionising voltage, and ion draw-out potential were maintained at 9.5 μA , 6.90 V and 1.9 V, respectively, with the ion-source temperature at 175° to 200°, daily calibration overcoming the effects of variations. Tabulated molecule-ion intensities of various hydrocarbons at an ionising voltage of 6.9 V show that aromatics and aliphatics should be detected at the levels of 0.1 and 2%, respectively. Interference from paraffins and naphthenes is shown to be generally negligible. The analysis of catalytic cracked naphthas, virgin naphthas and hydroformates, and propylene polymers is detailed and calibration coefficients are tabulated. Results of total olefins and total aromatics determined by both low-voltage mass-spectrometry and fluorescent-indicator adsorption are compared; the standard deviation for total olefins by the indicator-adsorption method is 0.63% (16 tests), whereas that for the mass-spectrometer results is 1.39% (24 tests). The standard deviation for total aromatics is 0.66% by fluorescent-indicator adsorption and 0.74% by mass spectrometer.

E. G. CUMMINS

183. Analysis of the aromatic fraction of virgin gas oils by mass spectrometer. S. H. Hastings, B. H. Johnson and H. E. Lumpkin (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1956, 28 (8), 1243-1247.—A method for the semi-quantitative determination of the major compound types (benzenes, naphthalenes, dinaphthalenes, naphthalenes, acenaphthenes, acenaphthylenes, phenanthrenes, pyrenes, chrysenes, benzothiophenes, dibenzothiophenes and naphthobenzothiophenes) in the aromatic fraction of virgin gas oils (boiling range 600° to 1000° F) has been developed. The mass-spectrometric equipment previously described (Lumpkin and Johnson, *Anal. Chem.*, 1954, 26, 1719) was used, with the constant-volume pipette method of sample introduction.

E. G. CUMMINS

184. Spectrographic determination of trace elements in lubricating oil by the "tangent method." Tomio Okada, Shigeo Nakai and Tsunehide Kohzuma (Res. Lab., Maruzen Oil Co. Ltd., Shimotsu, Wakayama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, 58 (9), 661-664.—When the intensity of spectral lines on a photographic plate is plotted against the log. of the time of exposure, straight lines of different gradients (θ) are obtained for the various amounts of an element. The log. of $\tan \theta$ is empirically proportional to the log. of concn. of the element. This fact was utilised for the rapid determination of Ba (for Ba naphthenate) and P (for tritolyl phosphate) in lubricating oil. The sample is placed in a shallow vessel; on its surface a carbon disc rotates about a horizontal axis, a part of which is kept under the surface. A high-voltage spark (0.8 mH, 0.0033 μF , preliminary discharge 60 sec.) is struck between the disc and a carbon rod. Several exposures (80, 100, 120, 140 and 150 sec.) are made for the intensity for each exposure to be

measured. The error is $\approx 4\%$ when the characteristics of the plate are calibrated and $\approx 12\%$ otherwise.

K. SAITO

185. Temperature tolerances in the analysis of coal. I. Berkovitch (Sci. Dept., National Coal Board, London). *Chem. & Ind.*, 1956, (31), 814-816.—It is suggested that a set of tolerances on the figures indicated by the temperature-measuring instrument can be chosen so as to lead to an accepted random error due to temperature variation alone. The factors influencing the choice are given, with a numerical example, and the advantages of tolerance quotation in all specifications, combined with emphasis on the specified figure, to avoid high random error and systematic bias, are discussed.

E. G. CUMMINS

186. A new semi-micro method for determining nitrogen in coal. M. Dermelj and L. Strauch (Chem. Inst. "Boris Kidrič," Slovenian Acad. Sci. and Arts, Ljubljana, Yugoslavia). *Vestn. Slov. Kem. Društva*, 1955, 2 (3-4), 77-82.—The use of MnO_2 (Lange and Winzen, *Glückauf*, 1953, 89, 24) as a catalyst for the estimation of N in coal by the Kjeldahl method is not recommended. Excess of MnO_2 oxidises NH_3 to N, and too little fails to destroy all the organic matter. Good results are obtained with a K_2SO_4 - HgSO_4 -Se (186:4:0.8) catalyst. The sample (0.1 g) and catalyst (9 g) are boiled with H_2SO_4 (8 ml) until clear (≈ 15 min) and then for a further 10 min. The soln. is cooled and diluted to a vol. of 50 to 100 ml, 34 ml of a soln. containing 360 g of NaOH and 15 g of Na_2S per litre is added, and the NH_3 is steam-distilled for 12 min. into a mixture of 24 ml of H_2O , 10 ml of saturated H_3BO_3 soln. and 8 drops of indicator (12 mg of methylene blue and 7 mg of methyl red in 100 ml of 96% alcohol). The cold distillate is titrated with 0.02 N H_2SO_4 to a violet colour. There is no blank correction, and an accuracy within $\pm 0.01\%$ of N is easily attained.

A. B. DENSHAM

187. Method of determining volatile matter in high-temperature coke. G. Lange (Inst. für Aufbereitung, Kokerei n. Briktierung der Rheinisch-Westfälischen Tech. Hochschule, Aachen). *Brennst.-Chemie*, 1956, 37 (7-8), 106-108.—A quartz test-tube containing the dried sample is placed in a vertical furnace and connected by a side-tube to a filter and weighed tubes for the gravimetric determination of the gases evolved. Water and CO_2 are absorbed directly, CO is oxidised by I_2O_5 and absorbed as CO_2 , CH_4 is oxidised by CuO and absorbed as H_2O and CO_2 . The apparatus is swept out with dry O-free argon and the furnace is heated to $875^\circ \pm 10^\circ$ for 60 min. The results increase with temp. and time of heating and are higher for water-quenched than for dry-cooled coke. The precision of duplicate measurements is usually within $\pm 5\%$ of the mean value.

A. R. PEARSON

188. Studies on coal-tar bases. X. Quantitative analysis of pyridine bases from coal tar by ultra-violet absorption spectroscopy. Kyosuke Tsuda, Masao Maruyama and Nobuo Ikekawa (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *J. Pharm. Soc. Japan*, 1955, 75 (11), 1309-1313.—Methylpyridines in the pyridine base fraction of coal tar were determined by u.v. spectroscopy. The β -picoline fraction (b.p. 141° to 145°) containing 2:6-lutidine, and β - and γ -picoline was analysed by measuring the extinction coeff. in cyclohexane at six wavelengths. The fraction of 2:4-lutidine (b.p. 156° to 160°) containing 2:4-

2:5- and 2:3-lutidine was similarly analysed in 0.1 N H_2SO_4 , as was the fraction of b.p. 169° to 171° containing *sym*- and 2:3:6-collidine and 3:5-lutidine. The results agree well with those obtained by i.r. spectroscopy, with slightly greater errors for *sym*-collidine and 3:5-lutidine.

K. SAITO

189. Quantitative determination of brilliant green by an iodimetric method. G. A. Vaisman and A. R. Filenko (Cent. Pharm. Res. Lab., "GAPU," Ministry of Health, Ukr. SSR). *Aptechnoe Delo*, 1956, 5 (3), 23-24.—The method is based on the reaction of brilliant green with iodine to form the periodide, $\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2\text{HI}_4\text{I}_2$. Procedure—Dissolve a weighed sample (0.05 to 0.1 g) of brilliant green in 10 ml of dil. H_2SO_4 in a 100-ml calibrated flask; add 25 ml of 0.1 N iodine soln., shake thoroughly and make the soln. up to 100 ml. Filter the soln. through cotton wool, rejecting the first 10 to 15 ml, and titrate the excess of iodine in a 25-ml aliquot of the filtrate against 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ soln.; 1 ml of 0.1 N iodine soln. \equiv 0.00593 g of brilliant green.

E. HAYES

190. Micro-sublimation of bases of the Naphthol AS series with a new hot-stage microscope. W. Kunze. *Textil-Praxis*, 1956, 11, 160-162.—A special microscope with a stage that can be heated and cooled has been introduced by Leitz. Its range is from -20° to 360° and the thermometer is easily removable. The whole device can be mounted on a ring stand. The temp. is raised 4° per min. with 110- or 220-V transformers. Thirty-three Naphthol AS (fast) bases were investigated and details are given of their colour reflection, transparency colour and sublimation form, and of the melting points of the recrystallised base.

CHEM. ABSTR.

191. The identification of the Naphthol AS bases by means of micro-sublimation. W. Kunze. *Textil-Praxis*, 1955, 10, 684-686.—Thirty photomicrographs of sublimed Naphthol AS (fast) bases are reproduced. The sublimates were obtained by a special micro-technique and may be readily identified under the microscope.

CHEM. ABSTR.

192. Determination of chromium in textiles. Anon. Shirley Inst. Test Leaflet: No. Chem. 23, 1956, 2 pp.—Two methods are given for preparing a soln. for titration with $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, with N-phenylanthranilic acid or ferroin as indicator. In the first the sample is wet-ashed, then heated further in a Pyrex-glass flask under refluxing conditions with at least a 10-ml excess of HClO_4 . When the colour of the soln. changes to the orange of H_2CrO_4 , the flask is immersed rapidly in cold water, and the contents are diluted with 30 ml of H_2O . The soln. is boiled to expel Cl, and made up to 100 ml with *M* H_2SO_4 for titration. In the alternative procedure the sample is dry-ashed and heated on a steam bath with 0.3 g of KClO_4 and 5 ml of conc. HNO_3 in a crucible covered with a watch-glass. When effervescence has ceased, the sample is evaporated to dryness, the residue is dissolved in 5 ml of H_2O , and again evaporated to dryness. The residue is dissolved and made up to 100 ml with *M* H_2SO_4 for titration. There may be interference from Mn.

A. M. SPRATT

193. Determination of antimony, copper or iron in textiles. Anon. Shirley Inst. Test Leaflet: No. Chem. 24, 1956, 4 pp.—The method is designed for the determination of fairly large quantities of Sb, Cu or Fe. In each case the metal is brought

into soln. in its higher valence state, then reduced by TiCl_3 in the presence of HClO_4 . The HClO_4 selectively oxidises the excess of Ti^{3+} and the reduced metal is determined by titration with standard oxidising agents. The titration is carried out with KBrO_3 for Sb, and ceric ammonium sulphate for Cu and Fe. Modifications are given for determining Sb in the presence of Fe or Cu, but the method is not suitable for Cu and Fe separately.

A. M. SPRATT

194. Determination of chromium, copper, iron and manganese in pigmented textiles. Anon. Shirley Inst. Test Leaflet: No. Chem. 25, 1956, 5 pp.—Chromium, Cu and Fe are determined in the presence of one another by oxidation to their highest valence by wet-ashing in the presence of excess of conc. H_2SO_4 and HClO_4 . They are then titrated successively with standard $\text{Ti}_2(\text{SO}_4)_3$ soln., various visual indicators being used. When Cr and Mn are present together, the Cr is separated by pptg. the hydroxides of Mn, Cu and Fe. The filtrate is titrated with $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ soln. The mixed ppt. is dissolved in H_2SO_4 and, after treatment with sodium bismuthate and Na_2CO_3 , the metals are successively titrated with $\text{Ti}_2(\text{SO}_4)_3$ soln.

A. M. SPRATT

195. Determination of unbleached sulphite pulp in newsprint. Ryoiti Senzuy (Res. Inst. of Sci. and Ind., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** (11), 922-924.—Lignin is present in unbleached newsprint as ligninsulphonic acid and combines with glycol chitosan (**I**) in a 1:1 ratio. Air-dried newsprint (2 g) is treated with 0.025 N NaOH (20 ml) to produce a slurry, which is shaken with N HCl (2 ml) and water (20 ml), then with 0.01 N **I** for 15 min. and filtered. The free **I** is back-titrated with 0.0025 N K poly(vinyl sulphate), with toluidine blue (0.2% aq. soln., 1 to 2 drops) as indicator. No appreciable adsorption of **I** by the pulp itself is observed when the concn. of HCl is > 0.03 N.

K. SAITO

196. A spectrophotometric method for the determination of cationic detergents. A. V. Few and R. H. Ottewill (Univ. Cambridge, England). *J. Colloid Sci.*, 1956, **11** (1), 34-38.—A spectrophotometric method for the determination of cationic detergents in aq. soln. of concn. of about 10^{-5} M is described. The method is based on a complexing reaction between the detergent and the dye Orange II, the prep. of which is described. The dye is insol. in CHCl_3 , into which the complex may be extracted quant. to give a soln. of λ_{max} 485 m μ . The intensity of the colour in the CHCl_3 soln. is proportional to the concn. of detergent, Beer's law being obeyed over the range studied. Satisfactory results were achieved with trimethyloctylammonium bromide ($\pm 5\%$), dodecyltrimethylammonium bromide, cetrimide, and dodecylpyridinium bromide ($\pm 2\%$). The method is not affected by the presence of salts in the detergent soln., or by changes of pH in the range 2.2 to 8.3.

C. A. SLATER

197. Rapid volumetric method for the estimation of mercury, copper, arsenic, etc., in complex mixtures such as antifouling pigments. I. K. C. Seal (Gov. Test House, Alipore, Calcutta). *J. Indian Chem. Soc., Ind. Ed.*, 1955, **18** (4), 209-214.—The volumetric estimation of HgO by titration with iodine soln. in KI in the presence of

NaHCO_3 is described. Both I and KI enter into the reaction. The error ranges between 0.05 and 1%. The method takes less than 2 hr. and is applicable in the presence of other substances such as Zn, Fe^{3+} , Cu^{2+} , Pb, As, NO_3^- , and small amounts of SO_4^{2-} .

O. M. WHITTON

198. The quantitative determination of caoutchouc additives. III. W. Scheele and C. Ilshner-Gensch (Caoutchouc Inst., Tech. Coll., Hanover, Germany). *Kautsch. u. Gummi*, 1955, **8** (3), WT55-59.—Conductimetric methods are extended to the determination of free S in vulcanising processes. *Procedure*—To an alcoholic soln. of S add an excess of KCN (approx. twice the theoretical quant.). Transfer to a pressure bottle, and heat at 80° for 8 hr., so that all the S is converted into SCN^- . To remove excess of CN^- , add HNO_3 in an amount equivalent to the KCN used, and pass a current of N for ≈ 2 hr. while the soln. is boiling gently. Now titrate the SCN^- conductimetrically with AgNO_3 . Thiuram disulphides may be estimated in the presence of S by conductimetric titration with CuSO_4 after the addition of quinol. Mercapto-benzothiazole (**I**) interferes with the determination of S, the sum of both being obtained. **I** may, however, be determined by conductimetric titration with alcoholic iodine soln. or NaOH soln., if certain precautions are observed, and the S is then obtained by difference.

H. A. FISHER

See also Abstracts 41, 75.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

199. Semi-micro flame-photometry of serum sodium and potassium. R. L. Dryer (Biochem. Dept., College of Med., Iowa State Univ., Iowa City, U.S.A.). *Clin. Chem.*, 1956, **2** (2), 112-116.—For the internal-standard type of flame photometer it is possible to choose the concn. of added lithium and the serum dilution in such a manner that a single dilution of a small amount of serum suffices for the determination of both Na and K. Stock soln. of Na (50 milli-equiv. per litre) (**A**), K (20 milli-equiv. per litre) (**B**) and Li (395 milli-equiv. per litre) (**C**) are prepared; 17, 14 and 11 ml of **A** are separately diluted with 5 ml of **C** to 500 ml to give working standards equivalent to 170, 140 and 110 milli-equiv. of Na per litre in the serum. Similarly 2, 1.25 and 0.5 ml of **B** are diluted with 5 ml of **C** to 500 ml to give working standards of 8, 5 and 2 milli-equiv. of K per litre. The test soln. is prepared by diluting 0.1 ml of serum with 0.1 ml of **C** to 10 ml with water and is used for the determination of both Na and K with the appropriate filters.

H. F. W. KIRKPATRICK

200. Flame-photometric determination of serum calcium. F. L. Humoller and J. R. Walsh (Veterans Admin. Hosp., Omaha, Neb., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (1), 127-133.—The proteins in up to 0.5 ml of serum are pptd. with trichloroacetic acid and aliquots of the filtrate are diluted with isopropyl alcohol to a concn. of 50% for flame photometry. *Reagents*—(i) Dissolve 31 g of trichloroacetic acid in water to 500 ml. (ii) Mix 500 ml of isopropyl alcohol with 300 ml of water

and 0.2 ml of Sterox SE. (iii) Prepare a stock standard soln. containing 150, 5 and 5 milli-equiv. of Na^+ , K^+ and Ca^{2+} , respectively, per litre. *Procedure*—To 0.5 ml of serum in a conical centrifuge tube add 4.5 ml of (i). Mix, centrifuge and dilute 2.0 ml of the supernatant liq. to 10 ml with (ii). Measure the emission at 422.7 $\text{m}\mu$ in a flame photometer. Prepare standards from 1.0, 0.8 and 0.6 ml of (iii), diluted when necessary to 1.0 ml with water. Make up each standard and a blank (1.0 ml of water) to 50 ml with 9 ml of (i) and sufficient (ii).

W. H. C. SHAW

201. The determination and distribution of lead in human tissue and excreta. S. L. Tompsett (Biochem. Lab., Northern General Hospital, Edinburgh, Gt. Britain). *Analyst*, 1956, **81**, 330-339.—The method previously reported (Tompsett *et al.*, *Brit. Abstr. A*, 1935, 1160) has been slightly modified, mainly in manipulative details. The ash of the suitably prepared and ignited sample is dissolved in HCl and an aliquot portion is extracted with ether in the presence of a Na diethyldithiocarbamate soln. After removal of ether, the organic matter in the extract is destroyed by heating with conc. H_2SO_4 and 100-vol. H_2O_2 , the residue is dissolved in HCl and the extraction process is repeated in the presence of Na citrate and KCN at pH 7.5 to 8, and organic matter is destroyed as before. The diluted digest (\approx up to 20 μg of Pb) is treated with specified amounts of ammonium acetate, H_2SO_4 , KCN and 10 ml of CCl_4 and a slight excess of a dithione reagent. The extinction of the CCl_4 extract is measured at 525 $\text{m}\mu$ (max. for Pb dithionite) and 620 $\text{m}\mu$ (max. for free dithione). It is then shaken with 0.1 N H_2SO_4 and its extinction is again measured at the same wavelengths. The difference between the extinctions before and after reversion indicates the amount of Pb present. The distribution of Pb in human tissues and excreta in both normal and pathogenic subjects is discussed, as well as the conditions in which mobilisation from the skeleton, where it is inert, into soft tissue, where it is toxic, occurs. Removal of excess of Pb in plumbism by means of chelating agents is also discussed.

A. O. JONES

202. Spectrophotometric determination of ethanol in blood. D. Monnier and M. Fasel (Univ. of Geneva, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (2), 141-148.—The ethanol is steam-distilled into an acid soln. of $\text{K}_2\text{Cr}_2\text{O}_7$ and the unreduced dichromate is determined by spectrophotometry at 366 $\text{m}\mu$. To ensure max. accuracy, instead of standard curves being used, a parallel determination was carried out with a soln. of ethanol in water of known concentration. The average error of the determination is about $\pm 3\%$.

A. TESSLER

203. The influence of amino acids on sugar determinations, particularly by the methods of Potterat and Eschmann, and Hadorn and Fellenberg. H. Hadorn and K. W. Bieffer (VSK Lab., Basle, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (1), 4-15.—The interference of amino acids in the determination of sugar is traced to two factors—an increase in the reducing power of the sugar and the pptn. of Cu_2O in more or less colloidal form, which passes through the filter and is difficult to centrifuge. The error is considerably reduced by using the compleximetric method of Potterat and Eschmann, in which the reagent consists of Na_2CO_3 , CuSO_4 and EDTA (disodium salt) in stoichiometric proportions. *Procedure*—Mix 10 ml of sugar soln.

with 10 ml of reagent, boil for 10 min., filter off the Cu_2O ppt., dissolve it in HNO_3 and titrate the soln. compleximetrically. Interference from simple amino acids is negligible, but histidine, arginine, cysteine and creatinine still cause major error. This may be reduced by clarification by the Carrez method (adsorption on to a zinc ferrocyanide ppt. formed *in situ*). The same considerations apply to the method of Hadorn and von Fellenberg, in which Fehling's soln. is used.

H. A. FISHER

204. Studies in detoxication. LXIX. The metabolism of alkylbenzenes: *n*-propylbenzene and *n*-butylbenzene with further observations on ethylbenzene. [Determination of hippuric acid in urine.] A. M. El Masry, J. N. Smith and R. T. Williams (Dept. of Biochem., St. Mary's Hosp. Med. Sch., London). *Biochem. J.*, 1956, **64** (1), 50-56.—The method of Gaffney *et al.* (*Anal. Abstr.*, 1954, **1**, 1594) for the determination of hippuric acid in urine is modified so that the stage of paper chromatography is eliminated. Urine collected during 24 hr. is acidified to a pH of 2 to 3 with HCl and then diluted to 200 ml. The dilute urine (1 ml) is extracted with ethyl acetate (5 ml) and, after being centrifuged for 2.5 min., the extract (1 ml), in triplicate, is evaporated to dryness in test-tubes (6 in. \times $\frac{3}{8}$ in.) in an oven at 110°. The dry residue (a trace of water here gives high results) is treated with a soln. (3 ml) of 7% *p*-dimethylaminobenzaldehyde in acetic anhydride and the mixture is heated in an oil bath at 120° (carefully controlled) for 0.5 hr., then cooled to room temp. Ethyl acetate (2 ml) is added and the yellowish-brown colour of the soln. is measured spectrophotometrically at 460 $\text{m}\mu$ against a control with water instead of urine. The calibration curve is a straight line. Large amounts of amino acids do not interfere. The effect of phenacetic acid is irregular but it does not interfere if present in amounts not greater than half that of the hippuric acid. The interference is less if the colour from hippuric acid is measured at 470 $\text{m}\mu$ instead of 460 $\text{m}\mu$.

J. N. ASHLEY

205. An enzymatic spectrophotometric method for the determination of pyruvic acid in blood. S. Segal, A. E. Blair and J. B. Wyngaarden (Nat. Inst. Health, Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (1), 137-143.—The rapid, sensitive and specific method described is based on the conversion of pyruvate into lactate in the presence of lactic acid dehydrogenase (I) and reduced diphosphopyridine nucleotide (II). The blood pyruvate level in normal fasting subjects is found to be between 0.39 and 0.86 mg per 100 ml. *Reagents*—(i) Phosphate buffer, 0.1 M, pH 7.0 to 7.4. (ii) A soln. of II, approx. 2 μmoles per ml. *Procedure*—Add 5 ml of blood sample to 5 ml of 7% aq. HClO_4 in a 15-ml centrifuge tube. Mix, centrifuge, remove the pptd. proteins and re-centrifuge the supernatant liquid. Place 2 ml of the clear supernatant liquid in a small beaker in an ice bath, and adjust to a pH of 3 to 4 with about 0.2 ml of 5 N KOH. Allow the ppt. (KClO_4) to settle for 10 to 15 min., or centrifuge. To 1 ml of the supernatant liquid in a spectrophotometer cell add 1 ml of (i), 0.05 to 0.10 ml of (ii), and water to 3 ml. Read the extinction at 340 $\text{m}\mu$ against a water blank; add 0.01 ml of a soln. of commercial I diluted (1 + 9) with 0.01 M aq. NaCl. Determine the extinction again after the reaction is complete (4 to 7 min.) and deduct from this any similar change in an enzyme blank. Standards are

prepared from dilute aq. pyruvic acid or sodium pyruvate.

W. H. C. SHAW

206. A micro-method for the estimation of serum bilirubin. K. M. Laurence and A. L. Abbott (Biochem. Dept., Path. Service, Portsmouth, England). *J. Clin. Path.*, 1956, **9** (3), 270-273.—To 2-9 ml of water add 0.1 ml of serum or plasma, 0.5 ml of diazo reagent, and 2.5 ml of absolute methanol. Mix, allow to stand for 30 min. at room temp. and measure the extinction at 520 m μ (green filter). Prepare an artificial bilirubin (I) standard by diluting 1 ml of stock phenolphthalein soln. (50 mg per 100 ml in ethanol) to 200 ml with 0.1 M Na₂CO₃-NaHCO₃ buffer (pH 10.0). The colour of the standard represents 8.5 mg of I per 100 ml of serum at the test dilution. If the I content of the serum is < 3 mg %, use 0.2 ml of serum with 2.8 ml of water. The standard graph was linear up to 25 mg % of I, and the recovery of I added to serum averaged 99%.

H. F. W. KIRKPATRICK

207. The paper chromatography of porphyrins. C. Michalec and A. Komarkova (Biochem. Zentrallab. Städt. Fakultätskrankh. Karlova Univ., Prague). *Naturwissenschaften*, 1956, **43** (1), 19.—The esters of uroporphyrin, coproporphyrin I and III and protoporphyrin IX are readily separated by ascending technique in a solvent mixture of toluene and 96% ethanol (10:0.1, v/v). For two-dimensional runs either kerosene-CHCl₃ (4:2-6) or kerosene-propanol (5:1) is recommended for the second direction.

E. KAWERAU

208. The estimation of N-n-butyl-N'-sulphanilylurea [carbutamide] in serum, urine and faeces. A. Häussler (Pharm.-wiss., Lab. der Farbwerke, Hoechst A.-G., Germany). *Arzneimittel-Forsch.*, 1956, **6** (7), 393-394.—The colorimetric determination described is based on the diazotisation of the sample and its subsequent coupling with K guaiacol-sulphonate. A yellow to yellowish-orange colour develops and the extinction values, obtained in 20 min., are reproducible.

C. A. SLATER

209. Quantitative "test-tube" paper chromatography [of amino acids]. G. Gorbach and H. Demmel (Tech. Hochsch. Graz, Austria). *Mikrochim. Acta*, 1956, (7-8), 1264-1276.—A quant. method of determining amino acids by eluting from the paper the spot formed by the ninhydrin-amino-acid reaction has been perfected. This is accomplished with a 0.025% soln. of ninhydrin in pyridine which dissolves both the ninhydrin-amino-acid compound as well as the amino acids themselves from the paper and then allows them to react at 60° to 70° instead of at 100°, thus diminishing the risk of loss. As ninhydrin-pyridine soln. does not react with ammonium salts, blank-free results can be obtained in the presence of NH₄⁺. Final absorptometric measurement, with the Gorbach capillary photometer (*Anal. Abstr.*, 1955, **2**, 3252), gives results having a mean error of $\pm 3\%$. Evidence for the high sensitivity of the method is given by comparison with Boissonas's results (*Helv. Chim. Acta*, 1950, **33**, 1975) whose extinction of $E = 0.155$ for 10 μ g of leucine was obtained by the present method with only 1.38 μ g. The construction of capillary pipettes capable of measuring 0.2 to 2 μ l of amino acids with an accuracy of $\pm 0.01 \mu$ l is described.

D. F. PHILLIPS

210. Quantification of the ninhydrin colour reaction as applied to paper chromatography. R. E. Kay, D. C. Harris and C. Entenman (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **63** (1), 14-25.—A detailed study is made of the requirements for obtaining accurate quant. results for amino acids on paper chromatograms with ninhydrin reagent. The effects of variations in time and temp. of heating, the concn. of NaOH in the reagent, the stability and absorption spectra of the colours, and recovery of known amounts of amino acids from urine, plasma and liver homogenates are investigated. It is recommended that Whatman No. 1 paper should be prepared for use by extraction with 95% ethanol-1.2 N acetic acid (1:1) for 10 min. The paper is allowed to drain, rinsed three times in H₂O and once in 95% ethanol, then allowed to drain and dried at 65°. Satisfactory results are obtained with all developing solvents commonly used except those containing HCl of concn. > 0.1 N, which affects the colours obtained. After development, the papers are dried for 20 min. at 65°, sprayed with reagent (0.5 g of ninhydrin and 0.5 ml of N NaOH, in a mixture of 75 ml of 95% ethanol and 25 ml of H₂O) until just translucent, and then dried at 65° for 22 min. The resulting purple bands are cut out and eluted in closed tubes by shaking with 5 ml of 71% ethanol. After centrifuging, the colour is read at 575 m μ against a blank prepared by similarly eluting a white piece of the same size cut from the chromatogram. Calibration is rectilinear for up to 10 μ g of amino acids and the usual error is $\pm 6\%$.

W. H. C. SHAW

211. Use of fluorescence at ordinary temperature as a method of chemical analysis: first application to amino acids. B. Rybak, R. Locket and A. Rousset. *Compt. Rend.*, 1955, **241**, 1278-1280.—The fluorescence of solid samples of amino acids, illuminated by u.v. radiation, is a means of identification. "Spectrograms" of L-alanine, DL-phenylalanine, L-tryptophan and glycine are reproduced and their significance is discussed. S.C.I. ABSTR.

212. A colorimetric method for the determination of tyrosine. E.-R. Fritze and H. Zahn (Heidelberg Univ., Germany). *Melliand Textilber.*, 1955, **36** (11), 1136-1139.—A routine method for the determination of the tyrosine content of natural fibres is described. *Procedure*—Place 10 ml of tyrosine soln. (H₂SO₄ hydrolysate), containing 1 to 3 mg of tyrosine, in a 100-ml measuring flask, add sufficient 30% H₂SO₄ to bring the amount of acid present up to 6 ml of 30% H₂SO₄, add H₂O to 25 ml, and then 10 ml of HgSO₄ soln. (150 g of HgSO₄ in a mixture of 300 ml of conc. H₂SO₄ and 1300 ml of H₂O); set aside for at least 5 hr. Add 8 ml of 0.2% NaNO₂ soln., and after exactly 7 min. make up to 100 ml and measure the extinction in a spectrophotometer, with a green filter with max. absorption at 530 m μ . The margin of error was found to be 2-6% for the determination of tyrosine in 220 to 230-mg samples of wool.

H. A. FISHER

213. Perchloric acid as a reagent for tryptophan, tyrosine and hydroxyproline in paper chromatography. K. V. Giri (Dept. Biochem. Indian Inst. Science, Bangalore, India). *Naturwissenschaften*, 1956, **43** (1), 18.—The reagent of Tauber has been modified as a dipping reagent for paper chromatograms. *Reagent*—To 100 ml of absolute ethanol is added 20 ml of 60% HClO₄. After dipping the

paper, dry at 60° for 10 min. Tryptophan produces an intense green-yellow fluorescence in u.v. light and quantities down to 1 μ g can be detected readily. For the detection of tyrosine and hydroxyproline, the paper is given a preliminary treatment with ninhydrin (2% ninhydrin in acetone), dried at 60° for 10 min., and then treated as described above. Tyrosine is revealed as an intense yellow area which appears brick-red in u.v. light. Hydroxyproline appears as a pale brick-red colour which looks brown or a darker brick-red in u.v. light. None of the other 24 amino acids tested gave a colour reaction. E. KAWERAU

214. Behaviour of tyrosine and cystine on paper chromatograms and their quantitative estimation. N. Subramanian and M. V. Lakshminarayan Rao (Div. of Quality Control, Central Food Technol. Res. Inst., Mysore, India). *J. Sci. Ind. Res., B, India*, 1955, **14** (11), 566-570.—The streaking of tyrosine and cystine on paper chromatograms with almost all solvents is traced to their sparing solubility in the aqueous as well as the solvent phases. Use of amino-acid solutions and of solvent systems rendered sufficiently acid (pH 1) helps to secure compact spots and adequate separations. Unidimensional development with buffered phenol (pH 1.0) on similarly buffered paper is satisfactory for the quantitative estimation of the amino acids. I. JONES

215. Micro-analytical determination of cystine and methionine. A. Holasek, H. Lieb and W. Merz (Pregl Lab., Univ. Graz, Austria). *Mikrochim. Acta*, 1956, (7-8), 1216-1218.—The apparatus developed by Kuhn *et al.* (*Ber. dtsh. chem. Ges.*, 1939, **72**, 407) has been modified so that, in addition to enabling the determination of thiol and methylthio groups to be carried out, it also permits determination of the alkoxyl groups. The apparatus (illustrated) may be obtained commercially. D. F. PHILLIPS

216. Further studies on the reactions of disulphides with sodium sulphite. [Determination of disulphides.] J. R. McPhee (Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1956, **64** (1), 22-29.—Methods are described for the determination of cysteamine (2-aminoethanethiol), homocysteamine (3-aminopropanethiol), cystine hydantoin, homocystine hydantoin, and diformylhomocystine, by allowing them to react with Na_2SO_3 and titrating the thiol formed with AgNO_3 . J. N. ASHLEY

217. The penetration of ornithine and citrulline into liver slices. [Determination.] J. R. Bronk and R. B. Fisher (Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1956, **64** (1), 106-111.—Methods are described for the concn. and separation by paper electrophoresis of ornithine and citrulline, and for their subsequent determination by the ninhydrin procedure of Harris *et al.* (*Ann. Hum. Genet., London*, 1954, **19**, 196). J. N. ASHLEY

218. Paper chromatography and polarography as a tool for the study of histidine metabolism in skin. Estimation of histidine and urocanic acid in human sweat. J. A. Král, M. Kátová, A. Ženíšek, E. Krejčí and I. Stolz (Med. Sch., Karlova Univ., Prague, Czechoslovakia). *Biochim. Biophys. Acta*, 1956, **20** (3), 567-568.—Paper chromatograms of 50 μ l of (undesalted) samples and of 25- μ l vol. with added known amounts of histidine (I) and urocanic acid (iminazolyacrylic acid) (II) are

developed with the upper layer of *n*-butanol-water-acetic acid (4:5:1) for 5 hr. I and II are detected with Pauly reagent and the amounts present estimated visually by comparison. A study is made of the polarography of II, which, in 0.5 M acetate buffer (pH 4.7) containing 0.5 M KCl and after removal of dissolved O, gives a cathodic reduction wave ($E_3 = -1.3$ V vs. the S.C.E.), from the height of which the concn. (up to 23 mg %) can be estimated. The reproducibility is within $\pm 10\%$ according to conditions. No significant differences were found between chromatographic and polarographic results for II. W. H. C. SHAW

219. The determination of δ -aminolaevulinic acid. L. Shuster (Nat. Inst. for Med. Res., Mill Hill, London). *Biochem. J.*, 1956, **64** (1), 101-106.—Two colorimetric methods, which are sensitive to 0.05 μ mole, are described for the determination of δ -aminolaevulinic acid. One method is based on condensation of the acid with ethyl acetoacetate in 2 N NaOH to form a product which gives a red colour with *p*-dimethylaminobenzaldehyde. The colour is extracted with ethyl acetate and is read in a colorimeter with a green filter (500 to 570 $m\mu$) or in a spectrophotometer at 550 $m\mu$. The mol. extinction coefficient in terms of δ -aminolaevulinic acid at 550 $m\mu$ is 11,500. The second method is a modification of the Jaffé picrate reaction and depends on the reaction of an alkaline picrate complex of δ -aminolaevulinic acid with HCl to give an orange-red colour, which is read in a colorimeter with a blue filter (450 to 500 $m\mu$), or in a spectrophotometer at 450 $m\mu$ against a reagent blank. The mol. extinction coefficient in terms of δ -aminolaevulinic acid at 450 $m\mu$ is 6300. The picrate reaction can also be used for identification of δ -aminolaevulinic acid on paper chromatograms. J. N. ASHLEY

220. Buffer composition in paper electrophoresis [of serum proteins]. C. B. Laurell, S. Laurell and N. Skoog (Malmö Hosp., Sweden). *Clin. Chem.*, 1956, **2** (2), 99-111.—Filter-paper electrophoresis of serum proteins with a conventional type of moist-chamber apparatus and a buffer soln. containing Ca^{2+} gives not only a clear-cut resolution of albumin, and α_1 - and β -globulins, but also a separation of the β -globulin into two fractions (β_1 and β_2^{Ca}) in the same run without any disturbing water flow. The composition of the buffer soln. for the electrode vessels is 1.38 g of barbitone (I), 8.76 g of sodium barbitone (II), and 0.384 g of calcium lactate (III), dissolved in water and diluted to 1 litre (pH 8.6); and for moistening the paper is 1.66 g of I, 10.51 g of II, and 0.384 g of III made up similarly. H. F. W. KIRKPATRICK

221. A modified method for protein separation by zone electrophoresis on a starch gel. P. Bernfield and J. S. Nisselbaum (Tufts Univ., Boston, Mass., U.S.A.). *J. Biol. Chem.*, 1956, **220** (2), 861-860.—A starch gel consisting of 3% of maize starch, 1.5% of additional amylose, 3% of Hyflo Super Cel, and an appropriate buffer solution is an improved supporting medium in zone electrophoresis for fractionation of plasma proteins. The gel can easily be cut into small sections so as to separate the protein zones obtained in the electric field. Electro-osmotic flow is negligible because of the low content of solids in the gel, and there is no interaction between the proteins and constituents of the gel. The method of working is given in detail, and two cells are described: a small-scale cell for the separation of 2 ml and a large cell for

fractionating up to 50 ml of a 5 to 10% protein solution.
J. N. ASHLEY

222. Electrophoretic partition of β -globulins in human sera by a non-ionic detergent. G. A. Lloyd and G. T. Stewart (Mayday Hosp., Croydon, England). *J. Clin. Path.*, 1956, **9** (3), 248-250.—Addition to sera of 0.4% (w/v) of a long-chain fatty alcohol-ethylene oxide condensate, "Lubrol W," resulted in a separation of one or more intermediate protein bands between the β - and γ -globulins when paper electrophoresis was carried out in 0.05 M barbiturate buffer, pH 8.6, in the conventional manner. The bulk of the α - and β -lipid is also moved to a corresponding position. The effect is ascribed to interaction of the long polyoxyethylene chain of the detergent with the lipid components of the α - and β -globulin complexes in sera.
H. F. W. KIRKPATRICK

223. A simple screening test for elimination of artifactually high-valued protein-bound iodine samples. H. M. Malkin (575 Byron St., Palo Alto, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (1), 124-126.—The rapid test described will detect contamination of serum samples with radiological contrast media containing I. *Reagents*—(i) Dissolve 527 g of KOH (85%) in water to 1 litre. (ii) Dissolve 50.62 g of $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ in a mixture of 100 ml of H_2SO_4 and 400 ml of water. Dilute to 1 litre. (iii) Dissolve 9.9 g of As_2O_3 and 2.4 g of NaOH in 100 ml of boiling water. Dilute to 700 ml, add 8.5 ml of 7 N H_2SO_4 and dilute to 1 litre. *Procedure*—Add 2 drops of (i) to 3 drops of serum in a test-tube (13 mm \times 100 mm). Cover the tube and place it in boiling water for 30 min. Remove the tube, add 0.5 ml of water to the contents, then 1.0 ml of (iii) and 1.0 ml of (ii). Mix, allow to stand for 5 min. and examine visually against a white background. Samples containing > 80 μg % of protein-bound I show partial or complete decolorisation, readily differentiated from normal serum.
W. H. C. SHAW

224. The effects of iodine on the ultra-violet absorbance spectra of thyroglobulin, casein and insulin. C. L. Gemmill (Med. Sch. Virginia Univ., Charlottesville, U.S.A.). *Arch. Biochem. Biophys.*, 1956, **63** (1), 192-200.—A study is made of the u.v. absorption of thyroglobulin in 0.02 N KOH and in 0.1 N HCl and of the effect of alkaline iodination on the absorption. Iodination of casein and of zinc insulin is shown to produce similar spectroscopic changes and the significance of these is discussed.
W. H. C. SHAW

225. Estimation of 5-hydroxytryptamine in the presence of adrenaline. J. D. Garven. *Brit. J. Pharmacol.*, 1956, **11**, 66.—Adrenaline and nor-adrenaline interfere with the estimation of 5-hydroxytryptamine by the isolated rat-uterus method. Mushroom juice, which contains a polyphenoloxidase enzyme, can be used to eliminate these interfering substances from tissue extracts. Tissues are double extracted with acetone, filtered and evaporated to dryness under reduced pressure at 30° to 35°. For the assay, the residue is dissolved in water, extracted with light petroleum to remove lipids, and the aq. extract treated with mushroom juice for 40 min. at room temperature. The solution is then assayed for 5-hydroxytryptamine on the atropinised rat uterus in the usual way.
G. F. SOMERS

226. A spectrophotometric micro-determination of choline. D. J. Kushner (Forest Insect Lab., Sault Ste. Marie, Ontario, Canada). *Biochim. Biophys. Acta*, 1956, **20** (3), 554-555.—A modification of the periodide method of Appleton *et al.* (*Anal. Abstr.*, 1954, **1**, 758) is based on the increase in extinction at 365 m μ , in 1:2-dichloroethane solution, produced by the interaction of I and choline. Calibration is rectilinear with up to 50 μg of choline. Acetylcholine, acetyl- β -methylcholine and tryptophan interfere, but 100- μg amounts of the 25 amino acids and related substances examined do not. *Reagents*—(i) Dissolve dried choline chloride in water (1 mg per ml) and dilute when required for use. (ii) Dissolve 2.5 g of I and 3.1 g of KI in water to 250 ml. (iii) Reflux 1:2-dichloroethane with zinc dust and NaOH. *Procedure*—To 2 ml of sample soln. containing > 50 μg of choline in a test-tube add 1 ml of (ii), shake and place in an ice bath for 20 min. Add 10 ml of (iii) and mix by passing a fine stream of N for 30 sec. Aspirate off the upper aq. layer, and exactly 2 min. after adding (iii) measure the extinction at 365 m μ . Treat choline standards prepared from (i) and water blanks similarly and deduct the extinction of the blank (about 0.100) from all readings on samples and standards.
W. H. C. SHAW

227. The photometric micro-determination of compounds of ribose, in particular ribonucleic acid. H. Langer (Inst. Med. Biol., Dtsch. Akad. Wissenschaften, Berlin). *Naturwissenschaften*, 1956, **43** (1), 19-20.—The orcinol reaction for pentoses can be used for the quant. determination of polynucleotides if the ribose content of the nucleotide has been correctly determined beforehand. Pure ribose, adenosine, guanosine and yeast adenylic acid give identical extinction curves when the results for the purines are calculated on their respective ribose content. The ribose of pyrimidines is only partly liberated under the conditions of the test reaction, and the low extinction values that are obtained render the method unsuitable for these compounds.
E. KAWERAU

228. A micro-colorimetric method for the determination of propane-1:2-diol phosphate. C. G. Huggins and O. N. Miller (Tulane Univ., New Orleans, La., U.S.A.). *J. Biol. Chem.*, 1956, **221** (1), 377-383.—Propane-1:2-diol phosphate is hydrolysed by intestinal alkaline phosphatase to propane-1:2-diol and H_3PO_4 , after which the glycol is oxidised by HIO_4 to acetaldehyde and formaldehyde. The acetaldehyde is selectively removed by aeration at pH 7.0 to 7.2 and is collected in a bisulphite trap. The acetaldehyde is then condensed with *p*-hydroxydiphenyl in conc. H_2SO_4 as described by Eëgrwe (*Brit. Abstr. A*, 1934, 171), and its concentration is determined colorimetrically by the modification described by Barker *et al.* (*Brit. Abstr. A*, 1941, 543), except that the copper-lime purification is not needed.
J. N. ASHLEY

229. The titration of some phosphatides and related compounds in a non-aqueous medium. J. E. Garvin and M. L. Karnovsky (Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Biol. Chem.*, 1956, **221** (1), 211-222.—An electrometric titration method is described in which the solvent system is 0.001 M KCl in 2-ethoxyethanol-water (99:1). The method is used for the titration of 1 microequiv. of a variety of phosphatides, fatty acids, and related compounds. It could be used for the

determination and identification of small amounts of lipid substances.

J. N. ASHLEY

230. Steroidal hormones. II. A new colour reaction and colorimetric determination of testosterone and its esters. Minoru Hosoi (Res. Lab., Teikoku Hormone Mfg. Co., 1604, Shimosakunobe, Kawasaki, Kanagawa Prefecture). *J. Pharm. Soc. Japan*, 1955, **75** (12), 1506-1511.—Testosterone (I) and its esters selectively react with FeCl_3 in H_2SO_4 to give a stable blue colour (limit of detection 3 μg). An acetone soln. of the sample is evaporated on a water bath, then in a vacuum desiccator; the residue is heated with 0.1% FeCl_3 in 70% H_2SO_4 (0.5 ml) and diluted with 50% H_2SO_4 . The extinction coeff. at 610 m μ is proportional to the concn. of I (10 to 80 μg). I is satisfactorily extracted from commercial oily injections or suspensions with light petroleum or CHCl_3 .

K. SAITO

231. Effect of time on fluorescing power of oestrogenic steroids. H. S. Strickler, R. C. Grauer and M. R. Caughey (Allegheny Gen. Hosp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1240-1243.—In certain concn. of H_2SO_4 the fluorescing power of four oestrogenic steroids decreases with time. Under these conditions, purified urinary extracts have a background fluorescence due to residual impurities which remains constant with time. Thus by measuring the decrease of the fluorescence of the sample, the apparent oestrogen content can be corrected for impurities.

G. P. COOK

232. Some factors influencing the estimation of urinary 17-ketogenic steroids. E. Diczfalussy, L. O. Plantin, G. Birke and A. Westman (Karolinska Sjukhuset, Stockholm). *Acta Endocrinol.*, 1955, **18**, 356-373.—Some of the variables affecting the estimation of urinary 17-ketogenic steroids by the method described by Norymberski (*Nature*, 1952, **170**, 1074) have been investigated and certain modifications described. The method is based on the oxidative fission of the corticosteroid side-chain with sodium bismuthate and estimation by the Zimmermann reaction. For the estimation of total 17-ketosteroids, take duplicate 8-ml aliquots from a 24-hr. collection of urine. Add 8 ml of glacial acetic acid and 2 g of sodium bismuthate and shake mechanically in the dark for 30 min. Add another 1 g of sodium bismuthate, shake for 60 min. and leave at room temperature, in the dark, overnight. Centrifuge and transfer 2.5-ml aliquots of the supernatant liquid into 20-ml tubes. To each tube add three drops of a 5% solution of NaHSO_3 , stir and dilute with 2.5 ml of water. Add 0.5 ml of conc. HCl and place in a boiling-water bath for 15 min. Cool, add 8 ml of freshly distilled ether and shake for 2 min. Remove the aqueous phase by suction, and wash the ether with 2.5 ml of water followed by 2.5 ml of 3 N NaOH . Treat the ether extract with approx. 30 pellets of NaOH and filter. Evaporate the ether and dissolve the dry residue in a freshly prepared mixture of *m*-dinitrobenzene and alcoholic KOH . Incubate the solution in the dark at 25° for 60 min., then dilute with 4 ml of absolute ethanol and read the colour in a Beckman spectrophotometer. With each series of determinations run two standards of dehydroepiandrosterone (approx. 30 μg) in such a way that the standards form the first and last tubes of the series. 17-Ketosteroids are estimated simultaneously on another aliquot by the micro-method of Vester-gaard. The difference in the two estimations

indicates the amount of ketogenic steroids yielding 17-ketosteroids on oxidation with sodium bismuthate. The principal 17-ketosteroid formed after oxidation of urine specimens by sodium bismuthate has been identified as 11-oxo-aetiocholanolone (aetiocholan-3-ol-11:17-dione).

G. F. SOMERS

233. Chromatographic and electrophoretic determination of corticosteroids. K. D. Voigt, W. Schroeder and I. Beckmann (Univ. Hamburg, Germany). *Acta Endocrinol.*, 1955, **18**, 325-341.—Methods for the fractionation of steroid mixtures by means of column and paper chromatography and paper electrophoresis are described. For ordinary clinical investigation, separation into several main fractions is adequate, and methods of isolating and identifying individual metabolites involve such difficulties that they are of restricted use. The results obtained from separation of adrenocortical and urinary extracts are reviewed, and special findings in some pathological conditions are reported.

G. F. SOMERS

234. Infra-red spectrographic analysis of corticosteroids. L. O. Plantin (King Gustav V. Res. Inst., Stockholm). *Acta Endocrinol.*, 1955, **18**, 351-355.—The infra-red spectrographic technique is useful for steroid identification. Only small amounts are required and the test material is not destroyed as in colour reactions. Methods for obtaining the infra-red spectrogram are described, with special reference to the use of an infra-red microscope. The substance to be analysed is ground to a paste with liquid paraffin and the suspension is placed on a sodium chloride plate and analysed in a horizontal position. Alternatively, the substance can be melted on a sodium chloride plate or deposited from a solution, when as little as 10 μg of the steroid can be used.

G. F. SOMERS

235. Indirect analysis of corticosteroids. III. The determination of steroidal dihydroxyacetones. J. K. Norymberski and R. D. Stubbs (Chem. Res. Lab., Rheumatism Res. Unit, Nether Edge Hosp., Sheffield, England). *Biochem. J.*, 1956, **64** (1), 168-175.—A method is described for the differential determination of "zinc resistant" (17:20-diols and 17:20:21-triols) and "zinc labile" (dihydroxyacetones) 17-ketogenic steroids. For the determination of these steroids in urine, the sample is mixed with acetic acid and zinc powder and refluxed for 1 hr. A sample of the cooled supernatant liquor is treated with sodium bismuthate and then the "zinc resistant" total 17-ketosteroids are determined by the Zimmermann reaction. The total 17-ketosteroids are previously determined after treatment with sodium bismuthate. The 17-ketogenic steroids are then determined by difference.

IV. A note on the role of chloride and urea in the bismuthate treatment of urine. J. K. Norymberski and R. D. Stubbs. *Ibid.*, 1956, **64** (1), 176-178.—The system sodium bismuthate- NaCl -dilute acetic acid oxidises 17-hydroxy-androstanes to 17-ketones; the oxidation is inhibited by urea. Treatment of human urine with sodium bismuthate-acetic acid, followed by reductive removal of surplus reagent and then treatment with hot HCl , does not oxidise 17-hydroxyandrostanes to 17-ketones or destroy the 17-ketones. The failure of urinary chloride to induce these reactions is due to the inhibitory effect of the native urea.

J. N. ASHLEY

236. Physicochemical detection and measurement of aldosterone in body fluids and tissues. R. Neher and A. Wettstein (CIBA A.-G., Basel, Switzerland). *Acta Endocrinol.*, 1955, **18**, 386-395.—A discussion is given of methods developed for the extraction of aldosterone from tissues, blood and in particular urine, and also the determination of this hormone in the extracts after preliminary purification with the aid of two combined paper-chromatographic systems and several indicators. The aldosterone content of tissues, blood and urine samples is stated.

G. F. SOMERS

237. Factors which interfere in the manometric assay of monoamine oxidase. N. H. Creasey (Ministry of Supply, C.D.E.E., Porton, Wilts., England). *Biochem. J.*, 1956, **64** (1), 178-183.—Various enzymes occur in washed rat-liver mitochondria which may modify the oxygen uptake during oxidative deamination of isopentylamine or tyramine. A buffered reaction mixture that contains the monoamine oxidase preparation, 0.01 *M* tyramine, 0.01 *M* semicarbazide and 10^{-3} *M* cyanide is suitable for the determination of monoamine oxidase activity. Under these conditions, one atom of oxygen is absorbed for each mol. of substrate oxidised and the oxygen absorbed at 30 min. is proportional to enzyme concentration.

J. N. ASHLEY

238. Modified milk-clotting procedure for determination of papain activity. O. Gawron and F. Drais (Duquesne Univ., Pittsburgh, Pa., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (4), 349-352.—A simple and rapid method is described for determining the protease activity of papain. The milk-clotting method of Balls and Hoover (*J. Biol. Chem.*, 1937, **121**, 737) is modified by reducing the volumes used (1.2 ml of buffered enzyme solution and 2 ml of dried milk suspension) and by the use of cysteine (1.588×10^{-2} *M*) to activate the enzyme. Both NaCl and $(\text{NH}_4)_2\text{SO}_4$ inhibit enzyme activity, but correction factors (determined with known concn. of the salts) can be applied to obtain true activities in soln. containing concn. of the salts up to 0.33 *M*.

S. C. JOLLY

239. Methods for the determination of cholinesterase activity in blood. C. Stumpf (Pharmakol. Inst., Univ. Vienna, Austria). *Z. Vitam.-Horm.-u. Fermentforsch.*, 1956, **8** (1), 36-48.—The cholinesterase activity of blood can be determined by measuring the change of pH as the substrate is hydrolysed, the fall in concn. of substrate, or the rise in concn. of the products of hydrolysis. The literature up to 1955 is reviewed. (66 references.)

A. R. ROGERS

See also Abstracts 35, 81, 152, 250, 281, 297, 301, 329.

Drugs

240. Identification of alkaloids and other basic drugs by paper partition chromatography. L. R. Goldbaum and L. Kazyak (Walter Reed Army Med. Centre, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1289-1290.—The method is based on the pattern produced by the R_F values at four different pH values. By the schematic arrangement of these R_F values, a tentative identification of an unknown basic drug can be made from chromatograms run simultaneously, each at a different pH. To avoid the problem of repro-

ducibility of R_F values, a control compound, codeine, is run on the chromatogram along with the unknown. R_F data for 44 drugs at various pH values are listed.

G. P. COOK

241. New method for the determination of individual alkaloids in mixtures of alkaloids. H. Trabert (Entwicklungslab. VEB Homöopharm. Dr. W. Schwabe, Leipzig, Germany). *Naturwissenschaften*, 1956, **43** (15), 351.—The alkaloids of a mixture are separated by a suitable chromatographic process and their complex with Dragendorff's reagent is developed on the paper. It is found that this complex reacts with acetic anhydride to form a stable and intensely coloured substance that can be easily eluted from the paper. The extinction of this reaction product is measured photometrically at 420 $m\mu$ against a blank prepared from an area of paper that does not contain the alkaloid. Standard soln. of individual alkaloids treated in the same way yield linear extinction curves which serve in the final calculation of the result.

E. KAWERAU

242. The spectrophotometric determination of narceine. A. H. Witte (Forensic Lab., The Min. of Justice, 's Gravenhage, Netherlands). *Pharm. Weekbl.*, 1956, **91** (16), 588-593.—The proportions of alkaloids present in a sample of opium may be indicative of its origin. The determination of the lesser alkaloids thus assumes fresh importance. Existing methods for narceine determination rely on the formation of a red colour by oxidation. By the present method, chlorine water is used as an oxidising agent and greater stability of the colour formed and better accuracy are claimed. *Procedure*—Into a 25-ml flask place 10 ml of a narceine soln. (containing 2.5 to 25 mg in ≈ 0.5 *N* HCl), add 5 ml of chlorine water, and after 5 min. destroy the excess of Cl by adding 5 ml of a 10% Na_2SO_3 soln. Make up to 25 ml with water (soln. A). Add 5 ml to a 25-ml calibrated flask, make up to vol. with saturated Na acetate soln. and set aside for 1 hr. Measure the extinction in a 1-cm cell at 510 $m\mu$, with 5 ml of soln. A, diluted to 25 ml with water, as a blank.

H. A. FISHER

243. Determination of micro quantities of alkaloids by amperometric methods. II. Titration of strychnine nitrate in an acidic solution with tungstosilicic acid. Tadahiko Ogawa (Faculty of Eng., Yokohama Univ., Minami-ku, Yokohama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (4), 535-537.—The previous work (*Anal. Abstr.*, 1956, **3**, 1846) was extended to the use of an HCl soln. Strychnine nitrate (I) is not reduced until -0.90 V vs. the S.C.E., whilst tungstosilicic acid (II) shows a marked reduction at -0.60 V. By the use of II soln., amperometric titration of I (5 to 50 mg) is effected at -0.70 V in $> N$ HCl with an error of $< 2\%$.

III. Titration of quinine sulphate, ethylcarbonate and hydrochloride with tungstosilicic acid in an acidic solution. Tadahiko Ogawa. *Ibid.*, 1956, **77** (4), 537-539.—A similar experiment was carried out with quinine sulphate (III), ethylcarbonate (IV) and hydrochloride (V). The polarographic reduction waves of IV and V start at -0.75 and -0.80 V, respectively; that of IV shows a plateau at -0.72 to -0.84 V. A satisfactory amperometric titration of these salts (0.25 to 40 mg of quinine) is effected at -0.75 V in 1 *N* to 3 *N* HCl with an error of $< 2\%$.

IV. Titration of atropine, brucine, phenazone, papaverine, veratrine and cocaine with tungstosilicic acid in an acidic solution. Tadachiko Ogawa. *Ibid.*, 1956, **77** (4), 540-542.—Similar experiments were carried out with sulphates or chlorides of various alkaloids, including atropine, brucine, papaverine, veratrine and cocaine, and with phenazone. Since no appreciable reduction wave of these compounds is observed at < -0.80 V, their amperometric titration with **II** is carried out at -0.75 V in > 0.5 N HCl (error $< 2\%$). K. SAITO

244. The paper-chromatographic separation of ergot alkaloids. J. Kolšek (Inst. Org. Chem., Univ. Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1956, (9), 1377-1388.—The method of Macek (*Pharmazie*, 1954, **9**, 420) has been further developed. R_F values have been obtained for individual alkaloids and mixtures and a study has been made of their dependence on pH. In addition to natural alkaloids, a decomposition product of ergotamine has been detected. C. A. SLATER

245. Microscopical investigation and identification of the ergot alkaloids. J. Kolšek (Univ. Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1956, (7-8), 1193-1210.—Because of the lack of specific chemical tests for the ergot alkaloids, a microscopical investigation on the micro hot-stage has been made with the object of ascertaining physical constants to enable these compounds to be fitted into the Kofler identification tables. As all ergot alkaloids decompose on melting, refractive index determinations of the molten substance were replaced by appropriate crystallisation reactions, and partial use of the crystal refractive index was made. In addition to several alkaloids not previously investigated microscopically, lysergic and isolysergic acid were also studied. The author's findings are fully tabulated. D. F. PHILLIPS

246. Chromatographic separation of digitalis glycosides. G. J. Rigby and D. M. Bellis (Dept. Pharm., Univ., Manchester, England). *Nature*, 1956, **178**, 415.—Several of the constituents of *Digitalis purpurea* have been separated by paper partition chromatography. Strips of Whatman No. 3 MM chromatograph paper (7.5 cm \times 55 cm) are passed through a 30% (v/v) soln. of ethanediol in methanol and blotted with Whatman No. 1 paper. Soln. of the glycosides and aglycones in ethanol are applied to the starting line and the strips are hung overnight in a chamber saturated with CHCl_3 . The mobile phase, CHCl_3 saturated with ethanediol, is passed down the strips. To prevent the ethanediol from separating, a fold of dry Whatman No. 3 MM paper is placed over the end of the strip before putting it in the trough. Loads of 0.5 mg can be chromatographed satisfactorily and the constituents recovered quantitatively after removal of the ethanediol by heating for two days in a current of air at 30° . Approximate R_F values are as follows—deacetyldigilanol B 0.05, deacetyldigilanol A 0.20, gitoxigenin 0.55, gitoxin 0.80, digitoxigenin 0.90, and digitoxin 0.95. The glycosides in alcoholic extracts of powdered digitalis leaves have also been separated and estimated. The same solvent system has been used for separating mixtures of coumarin and related compounds, before testing for root-growth inhibition.

O. M. WHITTON

247. Determination of penicillin in its compound preparations. S. G. Pligin and A. I. Ponomov.

Aptechnoe Delo, 1956, **5** (3), 19-22.—The penicillins in procaine penicillin are converted into the relatively stable hydroxamic acids and these are determined colorimetrically in the form of their copper salts. **Procedure**—Dissolve a weighed sample (≈ 0.1 g) of procaine penicillin in about 75 ml of water in a 100-ml calibrated flask. After the flask has been kept at 45° to 50° for 10 to 15 min., cool and make the contents up to 100 ml. Transfer an aliquot of this soln. to a test-tube (19 cm \times 2 cm) and dilute the soln. with water to a vol. of 3 to 5 ml. Add 4.5 ml of a mixture of N soln. of hydroxylamine hydrochloride and NaOH (pH = 6.0); after 3 to 5 min. add 1 to 1.5 ml of 2 N acetic acid soln. and 3 drops of a soln. of CuNO_3 (containing 5% of Cu), and shake the tube. Add 11.5 ml of isobutyl alcohol and mix the contents by gently rotating the tube. Allow the phases to separate for 1 to 2 min., add 0.5 ml of ethanol and carefully mix the contents of the tube by gentle rotation. Measure the colour of the extract in an absorptiometer fitted with a dark-red filter. Carry out a blank experiment to determine the intensity of the colour due to the reagents. For the determination of procaine penicillin, a calibration curve is constructed from results obtained on pure benzylpenicillin.

E. HAYES

248. Chemical methods for the determination of antibiotics. III. Colorimetric determination of tetracycline [with ammonium molybdate]. Kiichiro Kakemi, Toyozo Uno and Masayoshi Samejima (Pharm. Inst., Medical Fac., Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1955, **75** (8), 970-972.—The colorimetric determination of tetracycline (**I**) (< 1 mg per ml) with ammonium molybdate (**II**) was studied in the presence of oxytetracycline (**III**). **I** gives a yellow colour (max. absorption, 404 $m\mu$) on the addition of **II** in an acetate buffer (pH 4), and **III** becomes red. The colour is satisfactorily developed by keeping the mixture of **I** and **II** in a water bath at 60° for 15 min. The extinction coefficients of the red compound of **III** are empirically identical at 548 and 430 $m\mu$, and that of the yellow compound of **I** is negligible at > 540 $m\mu$. Hence a linear working curve is obtained when the difference in extinction coefficient at 430 and 548 $m\mu$ is plotted against the concn. of **I** in the presence of **III**. The results are in good agreement with those obtained by bio-assay.

IV. Colorimetric determination of tetracycline [with sodium tungstate and hydrogen peroxide]. Kiichiro Kakemi, Toyozo Uno and Noriko Miyake. *Ibid.*, 1955, **75** (8), 973-975.—A clear purple colour (max. absorption 530 $m\mu$) is obtained when **I** (200 to 500 μg per ml, 2 ml) is kept at 40° for 25 min. together with Na_2CO_3 - Na_2WO_4 (3 g of Na_2CO_3 and 0.4 g of Na_2WO_4 in 100 ml of water) (5 ml) and H_2O_2 (0.015%) (1 ml). Since the extinction coeff. of chlortetracycline (**IV**) under the given conditions is $\approx 4\%$ that of **I**, the colorimetric determination (error $< 2\%$) of **I** can be effected in the presence of **IV**. K. SAITO

249. The biological standardisation of adrenocortical extracts in the golden hamster. H. Kuchmeister and G. Assman (Univ. Hamburg, Germany). *Acta Endocrinol.*, 1955, **18**, 379-385.—Adrenalectomised golden hamsters appear to be particularly suitable for the assay of adrenocortical extracts. After adrenalectomy, death occurs within 9-5 days and accessory adrenal tissue does not develop. Weight and survival time provide objective measurements. A unit is suggested as the amount of

adrenocortical extract required per day to maintain the adrenalectomized golden hamster at a constant weight over a period of at least 14 days.

G. F. SOMERS

250. Turbidimetric estimation of heparin with protamine. G. Fekete (Dept. Pharmacol., G. Richter, Ltd., Budapest, Hungary). *Naturwissenschaften*, 1956, **43** (12), 279-280.—The heparin-protamine compound forms a turbid aq. suspension because of its poor solubility. By adding various amounts of heparin to a 1% soln. of protamine sulphate and measuring the turbidity photometrically after 3 min., a calibration curve can be constructed which is linear between 50 and 12 international units per ml concn. The method was compared with the U.S.P. XIV method and the results were in good agreement. E. KAWERAU

251. Pharmaceutical analysis by polarography. VIII. Assay of phenazone and its salts. Kazuo Matsumoto (Gifu Public Health Lab., 3-chome, Yatsuume-cho, Gifu). *J. Pharm. Soc. Japan*, 1955, **75** (8), 1001-1003.—The carbonyl group in the 5-position of the pyrazoline skeleton is reduced polarographically with difficulty. Phenazone (I) (10^{-2} to 10^{-4} M soln.) is nitrosated with 0.1 M NaNO₂ (1 ml) in 0.1 N H₂SO₄ (1 ml) at 23° to 28° (12 min.). The resulting 4-nitrosophenazone remains stable for 6 hr. and can be determined polarographically in a soln. of Na₂SO₄ in the presence of gelatin. The nitrosated I soln. is neutralised with 0.1 N NaOH (1 ml) and submitted to polarography after the addition of 1% gelatin (0.5 ml). Tablets are extracted with CHCl₃ and a suitable portion is similarly treated.

XII, XIII. Assay of sinomenine and dihydroxycodeinone. Kazuo Matsumoto. *Ibid.*, 1955, **75** (8), 1003-1006.—Sinomenine (II) and dihydroxycodeinone (III), each having a carbonyl group in the 6-position of the morphine nucleus, can be polarographically determined in 0.1 N KCl soln. of pH 5. The wave heights (E_1) = -1.24 and -1.22 V vs. the S.C.E. for II and III, respectively) are proportional to concn. within the range 5×10^{-3} to 5×10^{-5} M. Tablets (≈ 30 mg of II) are dissolved in ethanol (10 ml) and a portion is evaporated to be treated as described above. II is similarly determined in injections or in aq. soln. of powder in the presence of hydrocotarnine hydrochloride, papaverine hydrochloride, atropine sulphate and hyoscine hydrobromide.

XIV. Opium alkaloids of benzylisoquinoline type. Kazuo Matsumoto. *Ibid.*, 1955, **75** (8), 1006-1009.—Opium alkaloids of the benzylisoquinoline type having an aldehyde radical in the 1-position or a carbonyl radical in the 9-position, can be polarographically reduced at all pH values. Those that have radicals other than -CO- or -CHO in these positions fail to show polarographic waves. Thus cotarnine, narceine and papaverdine are polarographically distinguished from narcotine, gnoscopine, hydrocotarnine, codamine, cryptopine, laudanine, laudanidine, laudanidine and papaverine.

XV. Assay of nerve stimulants, amphetamine and methylamphetamine. Kazuo Matsumoto. *Ibid.*, 1955, **75** (8), 949-953.—Both amphetamine (IV) and methylamphetamine (V) (0.1 to 3 mg) can be quant. nitrated with a mixture of KNO₃ and H₂SO₄ (1 g of KNO₃ in 10 ml of conc. H₂SO₄) (1 ml) on a water bath (5 min.). (Rathenasinkam, *Analyst*, 1951, **76**, 115). The product is cooled, diluted with water (10 ml), neutralised with aq. NH₃ soln. (30%, 10 ml)

and extracted with CHCl₃ (3×20 ml). The CHCl₃ soln. is filtered and evaporated, and the residue is dissolved in acetone (2 ml). This soln. is mixed with M KCl (0.5 ml) and McIlvaine's buffer (pH 5) (2.5 ml) and submitted to polarography. The E_1 value for the first and second waves are -0.37 and -0.67 V for IV, and -0.41 and -0.70 V for V, respectively. This method is suitable for the determination of IV or V in the presence of Na benzoate, ephedrine and caffeine. K. SAITO

252. Ultra-violet absorption spectra of narcotics. C. G. Farmilo, P. M. Oestreicher and L. Levi (Food and Drug Lab., Ottawa, Canada). *Applied Spectroscopy*, 1956, **10** (1), 15-28.—Illustrations are given of 56 spectra as published in *Bull. Narcotics, U.N., Dep. Social Affairs*, 1954, **6**, 56. K. A. PROCTOR

253. Rapid method for the quantitative determination of hexoestrol. M. E. Shub and A. S. Vasilenko (All-Union S. Ordzhonikidze Chem.-pharm. Res. Inst.). *Aptekhnoe Delo*, 1956, **5** (3), 25-26.—Hexoestrol is determined by bromination in ethanolic solution; at 8° to 10° the reaction is quant. and complete in 2 to 3 min. *Procedure*—Dissolve a weighed sample (0.05 to 0.07 g) of hexoestrol in 25 ml of ethanol in a 250- or 300-ml conical flask fitted with a ground glass stopper; add 25 ml of 0.1 N KBrO₃ and 1 g of KBr. Set the mixture aside at 8° to 10° for 15 min. and add 20 ml of 10% H₂SO₄, previously cooled to the same temp. Shake the flask and set it aside at 8° to 10° for a further 2 or 3 min.; add 1 g of KI and 20 ml of water and, after 5 min., titrate the liberated I against 0.1 N Na₂S₂O₃ soln. Carry out a blank experiment at the same time. E. HAYES

254. Titration of drugs and chemicals in non-aqueous solutions. IX. Determination of amphetamine derivatives in glacial acetic acid. Tetsu Kashima (Nat. Hyg. Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (9), 1112-1114.—With the aid of a glass electrode, hydrochlorides of amphetamine derivatives [(+)-methylamphetamine, (-)-ephedrine, (±)-methylamphetamine and (±)-methylephedrine] can be titrated with HClO₄ in the presence of mercuric acetate in amount approx. equiv. to that of the organic base. Sulphates or phosphates should be converted into hydrochlorides before the titration, because H₂SO₄ and H₃PO₄ react as weak bases in glacial acetic acid. The titration can also be carried out with crystal violet as indicator with sufficient accuracy for practical purposes.

K. SAITO

255. Spectrophotometric determination of phenylmercuric acetate. A. Eldridge and T. R. Sweet (Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1268-1271.—Acidified aq. soln. of phenylmercury acetate exhibit absorption max. at 250, 256 and 262 mμ, the last two wavelengths being suitable for quant. measurement. To reduce the error caused by impurities, HClO₄ is added. Since the u.v. absorption curve is a modified benzene curve, benzene interferes strongly; Cl⁻ also interfere. The method is suitable for amounts of 0.01 to 0.1 g of phenylmercury acetate and is accurate to within $\approx \pm 1\%$. A study of various interferences is presented. G. P. COOK

See also Abstracts 22, 152, 168, 189, 230, 308.

Food

256. Analyses and evaluation of dietary salt mixtures. H. Hadorn and H. Suter (Lab. VSK, Basel, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (2), 122-140.—A number of proprietary salt mixtures, intended for use, instead of table salt, by persons who are on diets with a restricted intake or total absence of NaCl or sodium salts in general, were analysed. The ingredients are tabulated, and discussed in relation to the data given on the label. The methods used to estimate the various anions and cations, namely, K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , choline, Cl^- , phosphate, lactate, acetate, formate and citrate, are described. A. TESSLER

257. Application of the Koltthoff - Kruisheer method to the analysis of sugar mixtures. S. Gianferraria and E. Pascucci (Lab. Chim. Centrale delle Dogane e I.I. Rome, Italy). *Chim. e Ind.*, 1956, **38** (4), 297.—The previously described method (cf. *Anal. Abstr.*, 1956, **3**, 3479) is applied to the analysis of hard candies; some typical results are presented. C. A. FINCH

258. The routine determination of admixed chalk in flour. R. Sawyer, J. F. C. Tyler and R. E. Weston (Dept. Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1956, **81**, 362-366.—Two methods for checking the chalk (creta) content of flour are described. In the colorimetric method the diminution of colour of chloroanilic acid soln. by pptn. of its calcium salt is measured absorptiometrically against water at 540 m μ . Since the final soln. used for extinction measurement is usually turbid, the extinction is measured before and after removal of the colour with sodium dithionite. In the flame-photometric method the flour is heated with dil. HCl and acetic acid in an autoclave at 20 lb per sq. in., the hydrolysate is treated with $ZrO(NO_3)_2$ and aq. NH_3 to remove PO_4^{3-} , and the Ca is then determined in the flame photometer against a control soln. prepared from creta-free flour and a standard soln. of Ca in the same way. These methods are conveniently applicable to the routine examination of large numbers of individual samples. Results are compared with those of the gasometric method previously described (Fraser and Weston, *Analyst*, 1950, **75**, 402). A. O. JONES

259. The fluorine content of flour and creta [prepared chalk]. J. F. C. Tyler and R. E. Weston (Dept. Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1956, **81**, 375-376.—The determined values for the fluorine content of bulked flour samples for the first quarter of 1955 are quoted, each bulked sample representing a particular type of flour. Bulk samples of creta from two main supplies were prepared and examined similarly. The creta content of the flour ranged from 9 oz to the statutory 14 oz per sack. A wholemeal (100% extraction) flour (exempt from compulsory addition) contained 1 oz per sack. The fluorine content ranged from 0.3 to 1 p.p.m. The two creta samples contained 225 and 230 p.p.m., respectively. The fluorine content of the flour is thus mainly attributable to the creta added. A. O. JONES

260. Retention of hydrocyanic acid by cereals and flours. P. Desbaumes and J. Deshusses (Lab. Cantonal de Chimie, Geneva, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (2), 113-121.—The method of Robbie and Leinfelder (*J. Ind. Hyg.*,

1945, 136) for the determination of HCN in air was adapted for the determination of HCN retained by food products after fumigation of flour mills, etc. *Procedure*—A mixture of steam and air is passed through the sample and carries any HCN contained therein first into a condenser where the steam is eliminated and then into a soln. of phenolphthalein. The extinction of the resulting red colour is then measured colorimetrically. Traces of HCN could thus be determined in various cereals, grains, pulses, cocoa and flours even a considerable time after fumigation. A. TESSLER

261. Some applications of paper chromatography to the examination of meat extract. T. Wood (Bovril Ltd., 148 Old St., London). *J. Sci. Food Agric.*, 1956, **7** (3), 196-200.—An attempt was made to separate by chromatographic methods constituents of meat extract other than proteins and inorganic salts. The extracts were obtained by treating successive batches of meat with the same hot liquors and evaporating the mixture to a thick paste. The extract was dialysed to remove protein and submitted to electrolytic desalting to remove inorganic salts. Chromatograms were made on Whatman No. 4 paper (10 in. \times 10 in.) with butanol - acetic acid - water (60:15:25) as the main solvent, run for 7 hr. Developing agents (tabulated) were applied by dipping the sheets. For the detection of carnosine, anserine and methylhistidine, the use of ninhydrin (0.2%) in acetone containing a little pyridine, followed by heating at 110°, is recommended. By comparison of the chromatograms with experiments in which pure compounds were used, the constituents of the extract could be identified and an approx. estimation of the quantities present could be obtained from the intensities of the spots. About 30% of the extract was unaccounted for. D. G. FORBES

262. The determination of lactose in milk. F. H. Grimbleby (Reading Univ., England). *J. Dairy Res.*, 1956, **23** (2), 229-237.—From a study of the influence of different clearing agents operating at different pH values, it is concluded that the accuracy of lactose determinations is influenced mainly by the procedure used in the prep. of the protein-free milk-serum. Factors investigated include the completeness of protein pptn., the formation of lactose-protein complexes, and the degree of hydration of the protein coagulum. The use of a clearing reagent containing Zn acetate, tungstophosphoric acid and acetic acid is recommended. *Reagent*—Dissolve 25 g of Zn acetate and 12.5 g of tungstophosphoric acid in water, add 20 ml of glacial acetic acid and dilute to 100 ml with water. *Procedure*—To 40 ml of milk in a 50-ml calibrated flask add 5 ml of reagent, dilute to vol. without mixing and then shake vigorously. Filter through a dry paper into a dry flask and measure the optical rotation of the filtrate in a 2-dm tube in a polarimeter illuminated with sodium light. Calculate the corrected rotation (r) from the percentages of protein (P) and fat (F) by means of the expression—

$$r = \text{observed reading} \times \frac{100 - (P \times 0.84 + F \times 1.07)}{100}$$

The lactose hydrate content of the sample in g per 100 ml is then equal to $\frac{100 \times r}{52.5 \times l} \times \frac{100}{80}$, where l is the length of the polarimeter tube in dm.

W. H. C. SHAW

263. A comparison of the Gerber and Röse-Gottlieb methods for the determination of fat in milk. W. P. Crocker, D. I. Jenkins, A. L. Provan, F. J. Macdonald, S. J. Rowland and J. C. D. White (The Nestlé Co. Ltd., Hayes, Middlesex, England). *J. Dairy Res.*, 1955, **22**, 336-339.—In a collaborative investigation carried out on behalf of the British Standards Institution, the Gerber method (B.S. 696:1936) and the Röse-Gottlieb method (B.S. 1741:1951) for the determination of milk fat are compared on 208 samples of milk covering the range 2.5 to 6.0% of fat. The Gerber method gave results higher by 0.01, 0.05, 0.08 and 0.12% of fat on milks containing 3.0, 4.0, 5.0 and 6.0% of fat, respectively, and the following relationship was found between the Gerber percentage (G) and the Röse-Gottlieb percentage (RG)—

$$G = 1.036 RG - 0.097.$$

It is considered that, if the capacity of the Gerber milk-pipette was reduced from 11.04 ml of water to 10.94 ml, the two methods would give results in agreement on milk containing 3.6% of fat (the average for England and Wales), and results sufficiently accurate for most purposes in the normal range of fat content.

W. H. C. SHAW

264. Evidence of maltol and hydroxymethylfurfural/dehyde in evaporated milk as shown by paper chromatography. F. E. Potter and S. Patton (Pennsylvania Agric. Exp. Sta., Univ. Park, U.S.A.). *J. Dairy Sci.*, 1956, **39** (7), 978-982.—Separation and identification of maltol and hydroxymethylfurfuraldehyde is attained on Whatman No. 1 paper by the descending technique with isoamyl alcohol-5 N formic acid (1:1), isoamyl alcohol-conc. aq. NH_3 -water (30:15:5) and ethyl acetate-pyridine-water (5:2:7), in which the respective R_F values are 0.76, 0.76; 0.23, 0.64; and 0.79, 0.88. Equilibration is for 1 to 2 hr. and development for 6 to 18 hr. Six spray reagents are detailed. The two compounds were detected in autoclaved (120°, 2 hr.) milk and in commercial evaporated milk, but not in milk heated at 65-68° for 20 min.

W. H. C. SHAW

265. Variations in iodine value of milk fats. J. W. Mayhead and C. R. Barnicoat (Massey Agric. Coll., N.Z. Univ., Palmerston North, New Zealand). *J. Dairy Res.*, 1956, **23** (2), 238-247.—The wide variations in the iodine value of milk fat from grazing cows are found to be determined mainly by differences in the oleic acid content. Factors influencing the variations include individuality of the cow, stage of lactation, breed differences, diurnal and incidental (irregular) day-to-day effects, nature of the food and plane of nutrition. From the results of feeding an unsaturated vegetable oil it is shown that considerable proportions of unsaturated long-chain fatty acids of milk were derived from the oil, and it is concluded that herbage lipids may contribute materially to the production of milk fat of grazing cows.

W. H. C. SHAW

266. Modification of the refractive index method for the determination of foreign fats in dairy products. V. R. Bhalerao and F. A. Kummerow (Illinois Univ., Urbana, U.S.A.). *J. Dairy Sci.*, 1956, **39** (7), 947-955.—The method described is based on the glyceride content of butter fat and will detect $\pm 10\%$ of added foreign fat. The fat is first separated into fractions sol. and insol. in absolute ethanol at 20° and the n_{40}^D of the two fractions is measured. Any lowering of the n_{40}^D of the ethanol-

soluble fraction from the value for butter fat (1.4538 to 1.4541) suggests the presence of coconut oil, which can be confirmed by an estimation of the trisaturated glycerides remaining after treatment with KMnO_4 and acetic acid in acetone soln. Increase in the refractive index of the ethanol-insoluble fraction over the normal range (1.4539 to 1.4544) indicates the presence of other vegetable or animal fat. This fraction is further fractionated from acetone at 0° and the iodine value of the acetone-soluble portion is determined by the Wijs method. The iodinated oil is then extracted and its refractive index is compared with that for butter fat (1.4713 to 1.4732). The limitations of the various tests for adulteration of butter fat are discussed.

W. H. C. SHAW

267. A summary of methods for the detection of foreign fats in dairy products. V. R. Bhalerao and F. A. Kummerow (Illinois Univ., Urbana, U.S.A.). *J. Dairy Sci.*, 1956, **39** (7), 956-964.—Methods discussed include those based on the butyric acid, isovaleric acid, unsaturated fatty acid or tocopherol contents; on the phytosterol acetate, hydroxamic acid colour and azelaoglyceride tests; on the addition of indicator substances to hydrogenated fats; and on the glyceride composition of butter fat, including methods of selective solidification, crystallisation, critical soln. temp. and fractionation from ethanol. Results given with different adulterants show the limitations of the various tests.

W. H. C. SHAW

268. The estimation of the total volatile fatty acids in cheese. A. J. G. Barnett and G. A. Tawab (Aberdeen Univ., Scotland). *J. Dairy Res.*, 1956, **23** (2), 277-282.—The method described is based on Soxhlet extraction and micro-distillation of the volatile fatty acids. The results obtained compare well with those given by more lengthy methods. *Procedure*—Pass sufficient of the sample through a chilled mincer and grind 10 g of the minced sample (with a chilled pestle and mortar) with 3.5 ml of cold 10% aq. H_3PO_4 and 15 g of chilled sand (25 g for soft cheese). Transfer the mixture quant. to a Soxhlet apparatus with ether and extract with boiling ether for 8 hr. or overnight. Wash down the condenser with more ether and extract the total solvent by gentle shaking with six 25-ml amounts of 0.1 N NaOH. Note the total vol. of the 0.1 N NaOH extract and evaporate the ether from 25 ml of it in a beaker on a hot-plate. Transfer the extract quant. to a 25-ml calibrated flask and dilute to vol. with water. Distil 3 ml of the liquid in a micro-Kjeldahl apparatus in the presence of 6 ml of buffer (10% of K oxalate and 5% of oxalic acid). Filter the distillate directly into a flask; collect 80 ml, and titrate with 0.02 N NaOH (bromothymol blue) to give the water-soluble volatile fatty acids. The water-insoluble volatile fatty acids are determined by washing the condenser and filter with 10 ml of neutral ethanol (bromothymol blue) and titrating with 0.05 N NaOH.

W. H. C. SHAW

269. The determination of the coagulating power of commercial rennet extracts using an automatic tester. F. C. Storrs (United Dairies Res. Lab., Wood Lane, London). *J. Dairy Res.*, 1956, **23** (2), 269-276.—The apparatus described consists of a turntable rotated electrically at a low constant speed. A beaker containing the test mixture of milk and rennet at 37° is centrally placed on the turntable and a stainless-steel paddle is immersed eccentrically in the liquid. Deflection of the

paddle when the coagulation reaction is complete is detected electrically. Reproducibility is about 1% and the total experimental error with triplicates on one sample is < 2%. Details are given for the preparation of reference samples of rennet by freeze-drying, and of a reproducible substrate from spray-dried separated milk powder.

W. H. C. SHAW

270. Suitability of various methods to detect watering of buttermilk. F. Kiermeier and G. Firner (Chem. u. Phys. Inst. Süddeutschen Versuchs- und Forschungsanstalt für Milchwirtschaft Weihenstephan). *Z. Lebensmitt. Untersuch.*, 1956, **103** (6), 437-441.—The various methods—determination of ash content, freezing point, refractive index and density—for detection of the addition of water to buttermilk are critically examined.

S.C.I. ABSTR.

271. Determination of caffeine in various food-stuffs. J. Eisenbrand and D. Pfeil (Chem. Untersuchungsamt für das Saarland, Saarbrücken). *Z. anal. Chem.*, 1956, **151** (4), 241-258.—A spectrophotometric method, based on the extinction maximum at 273 m μ , for the estimation of caffeine (I) in coffee, tea, maté and cola is described. The molar extinction for I, after checking the spectrophotometer with KNO₃ solution, is given as 9342 (mean). For many purposes I can be estimated in extracts by direct spectrophotometry. The following correction gives good agreement in many cases with the gravimetric method— $E_{273} \text{ m}\mu$ (corrected) = $E_{273} \text{ m}\mu - \frac{1}{2}(E_{310} \text{ m}\mu + E_{245} \text{ m}\mu)$. A paper-chromatographic method with a solvent mixture of butanol - water - acetic acid (8:0.5:11.5), which separates I from trigonellin, is described; the I spots are detected by a u.v. lamp transmitting the 254-m μ Hg line, then extracted with water and estimated spectrophotometrically. A simple maceration with boiling water extracts < 94% of I from the samples.

P. S. STROSS

272. Determination of volatile acids in wine. E. Bohm (Pub. Anal. Lab., Hanau, Germany). *Dtsch. Lebensmitt. Rdsch.*, 1955, **51** (12), 286-287.—A novel apparatus for the steam-distillation of the volatile acids from wine is described. This incorporates a steam generator and distillation flask in one apparatus. A sample of 6 ml of wine is used for analysis, 60 ml of distillate being obtained; this is titrated with 0.1 N NaOH against phenolphthalein at just below boiling point, to give the volatile acids, calculated as acetic acid.

H. A. FISHER

273. An improved preliminary treatment for the routine estimation of lead in wines and related products. N. Greenblau and J. P. van der Westhuyzen (Gov. Chem. Lab., Cape Town, S. Africa). *J. Sci. Food Agric.*, 1956, **7** (3), 186-189.—The preliminary destruction of organic matter in wines, must, mineral waters and urine can be accelerated by the use of I₂O₅ as a supplementary oxidising agent, and enables the oxidation of the resulting carbonaceous masses to be more easily controlled. *Procedure*—Heat the wine sample (50 ml) in a 800-ml Kjeldahl flask to remove the alcohol. Add I₂O₅ (0.5 g) and boil for 10 min. Remove the flame and add conc. HNO₃ (25 ml) and evaporate to a low bulk. Repeat this operation with more conc. HNO₃ (25 ml). Wash the mixture into a 4-cm silica basin, evaporate on a medium hot-plate and finally ignite at a controlled temperature of 480° for 30 min. Cool, moisten the residue with conc. HNO₃, evaporate to dryness and re-ignite to a white ash in the

muffle-furnace. Cool the dish and wash the contents into a separating funnel with dil. HNO₃ (1%) (2 x 25 ml) and ammonium acetate soln. (20%) (5 ml). Extract the mixture with a little redistilled CHCl₃ to remove free I. Run off the CHCl₃ layer. Add hydroxylamine hydrochloride soln. (50%) (1 ml), citric acid soln. (50%) (2 ml) and 4 drops of thymol blue indicator (0.1%). Neutralise the soln. with conc. aq. NH₃ soln., add KCN soln. (10%) (1 ml) and dithizone soln. in CHCl₃ (0.0015%) (20 ml) and estimate the lead colorimetrically. The method gives results close to those obtained by the classical nitric - sulphuric acid digestion procedure.

D. G. FORBES

274. Detection and identification of fat-soluble coal-tar dyes in foods by extraction with acid mixtures and chromatography on impregnated paper. W. Lindberg (Hyg. Inst. der Univ., Oslo, Norway). *Z. Lebensmitt. Untersuch.*, 1956, **103** (1), 1-14.—The oil or fat (10 to 30 g) containing the colour is dissolved in light petroleum (60 ml), shaken in a separating funnel with acid (e.g., conc. HCl - water - glacial acetic acid) (15 ml). The acid - water phase is run into a second funnel containing water (25 ml), aq. NaOH soln. (5 ml) and ether (35 ml) and the colour is separated in the ether layer; this is washed free from acid and alkali, and the ether is driven off. The residue is saponified with alcoholic KOH, the unsaponifiable portion is isolated and dissolved in ethyl acetate (0.25 to 0.5 ml). The dye is identified by a chromatographic method on paper previously impregnated with liquid paraffin, the solvent liquid being methanol (80 vol.-%) with addition of acetic acid (5%).

S.C.I. ABSTR.

275. Determination of artificial dyes in foodstuffs and identification of the dyes by paper chromatography. I. Wines, vermouth, aperitifs, liqueurs, syrups and fruit juices. J. Deshusses and P. Desbaumes (Lab. Canton. de Chimie, Geneva, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (1), 15-19.—An improved modification of Arata's method is given. *Procedure*—Boil 50 ml of the wine sample till the vol. is reduced to about one half. Add 25 ml of water, 1 ml of N HCl and a thread of wool (50 to 60 cm long, \approx 0.2 g). Boil for 5 min., remove and rinse the wool and place it for 10 min. in 50 ml of boiling water containing 0.2 ml of N HCl. Repeat till the water stays colourless. Rinse and boil the wool in 30 ml of 2% aq. NH₃ for 10 min. Remove the wool and continue to boil the soln. till the NH₃ is removed. Make up to 20 ml with water, add 1 ml of N HCl and a thread of wool \approx 40 cm long, and boil for 5 min. Rinse the wool thread and place it into 10 ml of 2% aq. NH₃ for 1 hr. at room temp. Evaporate the resulting dye soln. to dryness, then add a few drops of water. Identify by ascending paper chromatography. For more accurate identification, two runs are made, with different solvents—2% aq. NH₃ saturated with isobutyl methyl ketone and acetone - H₂O - conc. HCl (10:40:1). It is claimed that 0.5 mg of synthetic dye (Bordeaux red in red wine or tartrazine in white wine) per litre of wine may be identified by this method.

H. A. FISHER

276. A rapid method for the estimation of unsaturation of fats and oils by use of hypochlorous acid reagent. S. Mukherjee (Univ. Coll. of Sci. and Technol., Calcutta, India). *J. Amer. Oil Chem. Soc.*, 1955, **32**, 351-353.—The method described has the following advantages—the reaction takes only

4 to 5 min., addition takes place in an aq. medium, conditions are uniform for any degree of unsaturation, and any secondary reaction, e.g., in the presence of hydroxyl groups, is insignificant. *Procedure*—Prepare the reagent by passing Cl gas through 4 N NaOH soln. at $< 10^\circ$. Store in amber bottles in a refrigerator and dilute to 0.1 N immediately before use. Weigh the oil into a 500-ml glass-stoppered bottle, add 10 ml of glacial acetic acid, shake, and add 25 ml of 0.1 N NaOCl reagent; again shake well and set aside in the dark for 4 to 5 min. Add 20 ml of 15% KI soln. and titrate the liberated I in the usual manner.

H. A. FISHER

277. Separation, identification and estimation of volatile fatty acids. N. Coppens (Lab. Pharm. and Med. Chem., Gent Univ., Netherlands). *Meded. Vlaam. Chem. Ver.*, 1955, **17** (6), 199-213.—A survey is given of methods for separating volatile fatty acids by distillation in steam and for their qual. and quant. determination by column and paper chromatography.

H. A. FISHER

278. Paper chromatography in the fat field. XVIII. Separation of hydroxylated and brominated fatty acids. 1. H. P. Kaufmann and W. H. Nitsch. *Fette u. Seif.*, 1956, **58** (4), 234-238.—The paper-chromatographic method previously described (*Anal. Abstr.*, 1955, **2**, 2557; 1956, **3**, 849) for the separation of saturated fatty acids, with paraffin as stationary phase and dil. acetic acid as mobile phase, is further studied and extended to hydroxylated and brominated fatty acids. For the separation of the acids from decioic to stearic, 90% acetic acid is best; for the acids from nonoic to myristic 80%, and for the lower acids 70%. Because of variations in R_F values with experimental conditions, myristic acid is used as a standard. With 90% acetic acid as mobile phase and either paraffin (boiling range 190° to 220°) or undecane as stationary phase, oleic, linoleic and linolenic acids can be separated in the presence of stearic acid, but the *cis-trans* isomers of long-chain unsaturated acids have about the same R_F values. The method is also successfully applied to the separation of mixtures of straight-chain hydroxy acids, and to mixtures of these with saturated acids; with 85% acetic acid as mobile phase, ricinelaidic and elaidic acids are easily separated. Fatty acids with a hydroxyl group close to the carboxyl are difficult to separate from the corresponding saturated acids, but they can be separated from the isomeric acids in which the two groups are remote from one another. Under the conditions used, brominated acids are more mobile than saturated acids, and the mobility increases with increasing bromine content.

E. HAYES

279. Detection of rape-seed oil in edible oils by paper chromatography. H. Hadorn and K. W. Biefer (Lab. VSK, Basel, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (2), 75-83.—To detect the adulteration of edible oils with rape-seed oil, advantage is usually taken of the fact that rape-seed oil contains a high percentage of erucic acid whereas other edible oils contain none. The basis of previous methods was either the low solubility in alcohol of the lead salt of this acid or the selective oxidation of the acid by means of an alkaline soln. of permanganate. For greater sensitivity, use was made of a modified form of the ascending paper chromatographic method introduced for the separation of higher fatty acids by Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557;

1956, **3**, 849). Erucic acid is detected through the appearance of a characteristic spot at the foot of the chromatogram. The presence of as little as 5% of rape-seed oil can thus be ascertained.

A. TESSLER

280. Chromatographic detection of oils of *Cruciferae* in admixture with vegetable oils. O. Priori (Provincial Chem. Lab., Turin, Italy). *Olii Min.*, 1956, **33**, 23-25.—A solution of the oil in benzene (1:1) is passed through an alumina column; after rejection of an initial benzene eluate, the methanol eluate is collected and the solvent evaporated. The fraction obtained (in methanol solution) is then subjected to chromatography (ascending) on paper impregnated with petroleum jelly, the spots of oil being revealed by means of iodine vapour. Rape and ravinon oils show five characteristic spots, whereas other oils such as olive and arachis give only two spots; 5% and even less of the former group may be detected in other oils.

L. A. O'NEILL

281. Separation of vitamin-A alcohol and vitamin-A esters by paper chromatography. E. Kaiser and B. M. Kagan (Michael Reese Hosp., Chicago, Ill., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **63** (1), 118-121.—Separation of 1 to 2- μ g amounts of vitamin-A alcohol, acetate and palmitate is attained on Munktel No. 20 filter-paper developed by the descending technique for 3 to 4 hr. with isopropyl alcohol-water (1:1). After being dried with hot air the paper is sprayed with a saturated soln. of $SbCl_5$ in $CHCl_3$. The method is applied to the examination of serum and tissues for vitamin A, and details for preparing extracts of these materials for chromatography are given. Vitamin A is found to be present mainly as the alcohol in serum and as higher fatty ester in liver.

W. H. C. SHAW

282. Maleic anhydride in the study of naturally occurring isomers of vitamin A. P. A. Plack (Nat. Inst. for Res. in Dairying, Univ. of Reading, England). *Biochem. J.*, 1956, **64** (1), 56-63.—Maleic anhydride reacts rapidly with all-*trans*-, 7-*cis*- and 9-*cis*-vitamin A, and only slowly with 11-*cis*-, 13-*cis*-, 9:13-di-*cis*-, and 11:13-di-*cis*-vitamin A. When maleic anhydride is added to a mixture of vitamin-A isomers in benzene at 25° , the "fast reacting" isomers react during the first 2 hr., and then measurement of the absorption at $618 m\mu$ in the Carr-Price test gives the amount of "slow reacting" isomers. The amount of "fast reacting" isomers can then be ascertained from the Carr-Price value obtained before addition of maleic anhydride.

J. N. ASHLEY

283. Quantitative determination of ascorbic acid. M. K. Abramov and Ya. K. Kadyrov (Tashkent Pharm. Inst.). *Aptechnoe Delo*, 1956, **5** (2), 28-29.—Ascorbic acid in aq. soln. is quant. oxidised by an excess of $K_3Fe(CN)_6$ in the presence of $ZnSO_4$ [to ppt. $Fe(CN)_6^{4-}$], and the unconsumed $K_3Fe(CN)_6$ is determined iodimetrically. Dextrose does not interfere.

E. HAYES

284. Colorimetric determination of ascorbic acid with 3:4-dinitrobenzoic acid. Tsunematsu Take-moto, Koji Daigo and Tadao Takai (Pharm. Fac., Osaka Univ., Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (8), 1025.—An experiment similar to that described in the previous paper (*Anal. Abstr.*, 1957, **4**, 162) was carried out with ascorbic acid; a yellow colour was produced in an acid soln. containing 3:4-dinitrobenzoic acid.

This coloured substance can be extracted with isomyl alcohol; Beer's law is obeyed (max. absorption 415 m μ) for < 0.6 mg of ascorbic acid.

K. SAITO

285. Determination of ascorbic acid in foodstuffs and biological materials. H. Moor (Hoffmann-La Roche & Co. A.-G., Basle, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (1), 20-27.—Available methods for determining ascorbic acid (I) are not sufficiently specific or sensitive. The author has now improved the method of Schmall *et al.* (*Anal. Chem.*, 1953, **25**, 1486) by using diazotised *o*-nitroaniline as colour reagent and by removing interfering impurities by extraction with isobutyl alcohol and light petroleum. The determination of I in milk powder is described. *Procedure*—To prepare the diazo reagent, dissolve 400 mg of *o*-nitroaniline in 20 ml of glacial acetic acid and make up to 250 ml with 3 N HCl; 1 ml of this soln. is mixed with 1 ml of 0.08% NaNO₂ soln. and 2 ml of isobutyl alcohol-ethanol (1:1). For the test, dissolve 6 g of milk powder in 100 ml of water in a 500-ml measuring cylinder, add 15 ml of 20% metaphosphoric acid soln., make up to 500 ml, and filter. The soln. should contain < 200 μ g of I. Place three 95-ml portions (A, B, C) of the filtrate into 200-ml stoppered measuring cylinders; to (A) add 5 ml of water; to (B) add an amount of standard soln. containing about the same quantity of I as the soln. under test. Make up to 100 ml. To the blank (C) add 5 ml of 0.02% dichlorophenolindophenol soln., when the soln. should become permanently pink. The three soln. are now treated alike. Extract each with 50 ml of isobutyl alcohol followed by 50 ml of light petroleum, place exactly 50 ml of extracted aq. soln. into a 100-ml separating funnel, and add 2 ml of diazo reagent. Allow to react for 5 min., then extract with 30 ml of isobutyl alcohol. To 25 ml of the isobutyl alcohol layer add 5 ml of 2% NaOH soln., shake vigorously to extract the dye formed in the aq. layer, centrifuge, discard the butyl alcohol and measure the colour of the aqueous alkaline layer at 540 m μ . It is claimed that 0.5 μ g per ml of I can be determined accurately by this method.

H. A. FISHER

286. An improved spot test for the detection of ascorbic acid in flour. K. J. Hayden (Novadel Ltd., St. Ann's Crescent, London). *Analyst*, 1956, **81**, 376-377.—The reagent described for the detection of ascorbic acid added as an improver to flour is the ferric-ferricyanide reagent of Tauber (*Brit. Abstr. A*, 1935, 903) modified by reduction of its acidity. A boiling soln. of FeSO₄ (1 g) in 50 ml of water and 10 ml of 85% H₃PO₄ is oxidised with KMnO₄ until a faint pink colour persists. A 20% NaOH soln. is added to the cooled liquid until a permanent turbidity appears, and this is just cleared with dil. H₂SO₄. The filtered liquid is mixed with 0.5 g of K₃Fe(CN)₆ dissolved in 100 ml of water. The surface of a smooth wet layer of the flour is covered with the reagent. In the presence of ascorbic acid, bright-blue spots or flecks appear in 1 or 2 min. Blue spots appearing after this time in flour that has been subjected to excessive chlorine treatment may be due to added reduced iron. Under a hand lens, spots due to ascorbic acid are irregular in shape and size, those due to reduced iron appear as blue spots surrounded by a diffuse ring.

A. O. JONES

287. The use of homocysteine in the estimation of dehydroascorbic acid. R. E. Hughes (Dunn Nutri-

tional Lab., Univ. of Cambridge, England). *Biochem. J.*, 1956, **64** (1), 203-208.—Homocysteine rapidly reduces dehydroascorbic to ascorbic acid at pH values above 6.8, and the ascorbic acid can be estimated by the reduction of 2:6-dichlorophenolindophenol without appreciable interference from the excess of homocysteine provided that the reaction is carried out within 30 sec. at pH 2.5. A routine method, based on this, is described for the determination of dehydroascorbic acid which is more rapid and specific than other available methods. It involves titration with 2:6-dichlorophenolindophenol before and after reaction with homocysteine. When interfering substances are present, the specificity is further increased by titration with and without addition of boric acid which, at pH 7, rapidly and completely destroys dehydroascorbic acid but is without effect on some of the interfering compounds.

J. N. ASHLEY

288. Microbiological and chick assay of vitamin-B₁₂ activity in feed supplements and other natural products. W. L. Williams, A. V. Stifley and T. H. Jukes (American Cyanamid Co., Pearl River, N.Y., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (4), 364-367.—A comparison has been made of four methods for determining vitamin B₁₂ in various crude products—(i) the *Escherichia coli* pad plate method, (ii) a modified method of the U.S.P. with *Lactobacillus leichmannii*, (iii) a microbiological method with *Ochromonas malhamensis*, and (iv) a chick-growth method. Methods (i) and (ii) determine both cobalamins and pseudocobalamins (substances that promote the growth of certain micro-organisms but not the growth of animals), but methods (iii) and (iv) determine only cobalamins. Most animal feeding supplements do not contain pseudocobalamins to any great extent, and method (ii) gives reliable estimates of their growth-promoting activity in animals, although at least one test with methods (iii) and (iv) should be performed.

S. C. JOLLY

See also Abstracts 75, 164, 165.

Sanitation

289. The determination of potassium and sodium in drinking water with the aid of the flame photometer. E. L. Molt and T. L. Hien (Lab. Rotterdamse Drinkwaterleiding, Rotterdam, Netherlands). *Chem. Weekbl.*, 1956, **52** (18), 313-316.—The amount of K and Na in drinking water is assuming increasing importance because of the radioactivity of natural K and the increased medical importance of these two elements. The authors studied the influence of Ca and Na on the results obtained for K, and of Ca and K on those obtained for Na. For the determination of K, interference from Ca and Na varies when these are present in low concn., but reaches a constant value for amounts of Na > 100 mg and of Ca > 50 mg per litre. For the determination of K, add 10 ml of a soln. containing 0.3% of Ca²⁺ and 0.2% of Na⁺ as chlorides to 100 ml of a soln. containing 1% of K⁺ as KCl to calibrate the instrument; add the same amount when making the determination. Accurate and reproducible results for K⁺ are claimed with this procedure. In the determination of Na⁺, there is interference from K⁺, but not from Ca²⁺, and 100 mg of K⁺ per litre of sample should be added. Anions do not affect the results of the flame-photometric determination of K⁺ or Na⁺.

H. A. FISHER

290. Studies on mineral springs. I. Determination of sodium ion by flame spectrophotometry. Morizo Ishidate, Yasushi Mashiko and Yasuo Kanroji (Chem. Dept., Hot Spring Res. Centre, 2-600, Kashiwagi, Shinjuku-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (12), 1492-1495.—The effect of anions and free acids on the flame-photometric determination of Na (< 20 milli-equiv. per litre) was studied with samples from various mineral springs. Sulphate, carbonate and bicarbonate ions decrease the intensity of the D-line by 2 to 3%. The sample should be boiled at pH 4 (to remove H₂S and CO₂), passed through a column of Amberlite IRA-410 (Cl), and the eluate submitted to flame photometry. Satisfactory results are obtained for most mineral springs other than those containing a significant amount of Fe³⁺, Al, or free H₂SO₄. K. SAITO

291. Improved rapid colorimetric micro-determination of dissolved oxygen. W. F. Loomis (The Loomis Lab., Greenwich, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1347-1349.—Comparison of the Loomis colorimetric method for determining dissolved O in 0.5-ml samples (*Anal. Abstr.*, 1954, **1**, 1382) with the standard Winkler method shows that the calibration curve is not strictly linear. By adapting the spectrophotometer to receive the airtight syringe even when its needle is still attached, by filling the syringe with reagent only to the 0.40-ml mark before filling with the sample, and by measuring the extinction at 586 mμ, a strictly linear curve that passes accurately through the origin is obtained. Other refinements make it a rapid alternative to the Winkler procedure; the coeff. of variation between the two methods is 2.5%. W. J. BAKER

See also Abstracts 41, 83, 84, 98, 99, 100, 143.

Agriculture and Plant Biochemistry

292. Chemical and biological determination of copper in soil. A. Henriksen (State Lab. Soil & Crop Res., Vejle, Denmark). *Nature*, 1956, **178**, 499-500.—*Procedure*—Air-dried soil (10 g) is shaken for 1 hr. with 0.02 M EDTA (100 ml), and the suspension is filtered after being set aside for 1 hr. To an aliquot of the filtrate, containing > 50 μg of Cu, are added approx. 10 ml of 1 M ammonium citrate soln. and, after thorough shaking, a further 1 ml of a 1% soln. of Na diethyldithiocarbamate and 15 ml of CCl₄. The mixture is shaken and then left to stand until the aq. phase separates completely from the CCl₄ phase. The latter is filtered before measuring its extinction with a Beckman DU spectrophotometer at 440 mμ and with a 10-mm cell. Results for the chemical and the biological method are compared. The EDTA extraction method removed on the average the same amount of Cu from the soil as did the growth of *Aspergillus niger*, the agreement being best in the Cu range of 1.0 to 1.5 p.p.m., and five times as much as did the HCl extraction. O. M. WHITTON

293. Analytical applications of the complexones. V. Determination of molybdenum in soils. F. Bermejo Martinez and A. Prieto Bouza (Anal. Chem. Lab., Fac. of Sci., Santiago de Compostela, Spain). *Inf. Quim. Anal.*, 1956, **10** (4), 123-131.—A method is described whereby the effect of interfering substances, which cause inaccuracy in the

KSCN-SnCl₂ colorimetric determination of Mo, is eliminated in one step instead of requiring a series of tedious eliminations. A 5-g sample of air-dry soil is calcined in a platinum dish at 450° for 3 hr., cooled, treated with 10 ml of water and 2 ml of conc. H₂SO₄, and the SiO₂ is removed by adding conc. HF and heating gently. The H₂SO₄ is removed by heating and the residue is dissolved in HCl (1:1), filtered, and the soln. evaporated. The residue is dissolved in constant-boiling HCl and 5 ml of saturated NaF soln. is added with sufficient EDTA (disodium salt) to chelate with the interfering cations (0.19 g per milli-equiv.). The soln. is boiled for 10 min., cooled and diluted with water to 45 ml, and shaken for 2 min. with 3 ml of a mixture of equal vol. of CCl₄ and amyl alcohol. Excess of solvent mixture is removed and 1 ml of 40% KSCN soln. is added, followed by shaking and the addition of 3 ml of a 40% soln. of SnCl₂·2H₂O in 20% HCl. After further shaking, 5 ml of the solvent mixture is added and shaking is continued for 2 min. The stem of the separating funnel is then washed with water and dried in a current of air. The funnel is inverted, the tap is opened and the orifice dried in a current of air. The tap is replaced and shaking is resumed. The mixture is allowed to stand for 15 min. and a few drops of the organic layer are discarded before measuring the extinction of the remainder at 465 mμ. A simultaneous blank determination is made and the result compared with a calibration curve prepared with a standard soln. of Mo. D. LEIGHTON

294. The determination of phosphoric acid in fertilisers. G. Sánchez Marco (La Ind. Química de Zaragoza, Soc. Anon., Spain). *Inf. Quim. Anal.*, 1956, **10** (4), 132-142.—The methods developed, used and recommended by different official bodies are reviewed. D. LEIGHTON

295. The determination of boron in boron-containing fertilisers. H. Wiele (Kali-Chemie A.-G., Hanover, Germany). *Z. anal. Chem.*, 1956, **151** (4), 270-273.—The separation of boron by distillation of methyl borate is not necessary in the colorimetric determination of boron with carminic acid in the absence of nitrate. There is no interference from Fe³⁺ and NH₄⁺; small quantities of PO₄³⁻ are tolerated but large quantities must be removed. To determine boron in superphosphate or pyrophosphate, shake a 5-g sample with water (250 ml) for 30 min., add 10% FeCl₃ soln. (60 ml) and CaCO₃ (5 g), then dilute to 500 ml and filter. Dilute an aliquot to 100 ml with 20% H₂SO₄ and add an aliquot (2.5 ml containing about 100 μg of borax) of this mixture to 0.1% carminic acid soln. in conc. H₂SO₄ (20 ml) and dilute to 25 ml with conc. H₂SO₄. Set aside for 1 hr. and measure the extinction. P. S. STROSS

296. Determination of nitrofurazone in cattle foods. H. J. M. van Zijl and N. Goossens (Rijkslandbouwproufstation, Maastricht, Holland). *Chem. Weekbl.*, 1956, **52** (33), 624-625.—The method described is claimed to be more rapid than that of Ellis *et al.* (*J. Ass. Off. Agric. Chem.*, 1953, **36**, 417). The nitrofurazone is extracted at room temp. with acetone which has the advantage over ethanol of not dissolving vitamin B₂; interfering substances are removed by oxidation with KMnO₄ and the nitrofurazone is determined spectrophotometrically. Reagents required are—(i) 0.5 g of KMnO₄ in 100 ml of water, (ii) 2% H₂O₂, (iii) acetone

(pure), (iv) a buffer soln. of 25 g of Na acetate and 18.5 ml of 50% acetic acid made up to 500 ml with water (pH approx. 4.7), (v) 100 ml of (iv) made up to 500 ml with acetone, (vi) a standard soln. of 0.02 g of nitrofurazone in 50 ml of acetone; of this soln., 0.2 to 1.0 ml is made up to 50 ml with acetone buffer (v). For the determination, 5 g of the cattle food is shaken for 15 min. with 50 ml of acetone, then filtered. A 25-ml portion of the filtrate is placed in a 50-ml calibrated flask with 10 ml of buffer (iv) and 2 ml of KMnO_4 and shaken for 1 min.; 1 ml of H_2O_2 is then added and after being shaken for another min. the flask is set aside for 5 min.; then the contents are filled up to the mark with the acetone buffer and filtered. If necessary dilute this soln. with acetone buffer so that there is from 100 to 400 μg of nitrofurazone in 50 ml. The extinction is measured in a 1-cm tube at 368 $\text{m}\mu$.

P. HAAS

297. Isolation and identification of parathion in biological material. A. Fiori (Ist. Med. Legale Assicurazioni, Univ. Padua, Italy). *Nature*, 1956, **178**, 423-424.—The organ (10 g) is homogenised in a mortar with quartz, then diluted with 20 ml of H_2O , 20 ml of ethanol, and 50 ml of 20% trichloroacetic acid. The mixture is shaken for 30 min., then a portion is centrifuged for 15 min. The supernatant liquid is filtered, the alcohol is evaporated and the aq. acid soln. is then filtered through a column of acid alumina prepared according to the method of Kuhn and Wieland (*Ber.*, 1940, **73**, 962). Parathion, which is completely adsorbed, is then eluted from the desiccated alumina with ethyl ether, and the eluate is filtered and evaporated with a weak air current. A soln. of the residue in benzene or alcohol and test spots of parathion and *p*-nitrophenol are placed on S. & S. 2043b paper (28 cm \times 25 cm) for chromatography. The ascending method of development is used with a solvent of 5% ethyl ether in water-saturated light petroleum. The paper is saturated overnight in the vapour of the water phase of the solvent. The run takes 2 to 3 hr. at 20°. Parathion, even 0.5 μg , is detected by a u.v. lamp at 2537 \AA , and the breakdown product, *p*-nitrophenol, at 3600 \AA . The parathion has an R_F value of 0.98 and *p*-nitrophenol one of 0.30. As a control, strips are cut from the chromatogram and examined in u.v. with an adapter for the Beckman DU spectrophotometer, first at 3200 \AA (max. for *p*-nitrophenol) and then at 2780 \AA (max. for parathion). O. M. WHITTON

298. Determination of cycloheximide (Actidione) residues in cherries. G. C. Prescott, H. Emerson and J. H. Ford (Upjohn Co., Kalamazoo, Mich., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (4), 343-345.—By introducing a preliminary extraction stage, the microbiological assay described by Whiffen (*J. Bact.*, 1948, **56**, 283) for cycloheximide will determine as little as 0.04 p.p.m. of the antibiotic in cherries. *Procedure*—The sample (500 g) of macerated fruit is heated under reflux for 45 min. with 300 ml of CHCl_3 , the mixture is cooled, and 250 ml of the CHCl_3 is evaporated to between 10 and 20 ml on a steam bath. The remainder of the solvent is removed by a current of air at room temp., the dry residue is suspended in 1 ml of ethanol, and the mixture is diluted with 9 ml of water. If the amount of antibiotic on only the outside of the fruit is required, the sample of whole cherries is soaked overnight in sufficient water to cover them (about 300 ml), and the water is decanted and extracted with 200-, 100-, 50- and 50-ml

portions of CHCl_3 . The combined CHCl_3 extracts are evaporated and the residue is dissolved as before. The soln. are then assayed microbiologically, a sufficient no. of replicate assays being used to obtain the required confidence limits. The content (p.p.m.) of cycloheximide in the fruit is given by—(microbiological result, μg per ml of aq. soln.) \div ($50 \times 0.772 \times 0.75$). The factors 0.772 and 0.75 are empirical factors based on recovery experiments and the distribution coefficient of cycloheximide between CHCl_3 and water. Ferbam and captan interfere, but dieldrin, methoxychlor, lead arsenate, basic Cu and glyodin do not.

S. C. JOLLY

See also Abstracts 29, 107, 162, 163, 288.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

299. [Glass] apparatus with liquid joints. G. Rey-Coquais. *Chim. Anal.*, 1956, **38** (8), 289-290.—The use of automatically operating liquid joints to replace stoppers or ground glass joints in reflux-extraction or -distillation flasks in the laboratory is described and discussed. The lower end of the distillation column is kept cold by the downward flow of H_2O from the usual inlet, complete annular closure of the joint (0.5 mm wide) between column and flask being effected by the liquid film formed by condensation of the vapour filling the joint. The limitations of this device and the precautions to be observed are stated. Its max. effectiveness is for the prolonged refluxing of acid or alkaline soln., e.g., dissolution of alloys, ores, etc. W. J. BAKER

300. Stirrer assembly for use under pressure. V. R. Shellman and B. J. Magerlein (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1359-1360.—A seal is described which permits the introduction of a stirring shaft into a vessel required for a chemical reaction under pressure. The semi-ball joint has been successfully used for pressures of up to 20 lb per sq. in.

P. T. BEALE

301. Syringe mechanism for simultaneous blood sampling at constant rates. J. C. Rose and P. Pfaff (Nat. Bureau Standards, Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (1), 134-136.—An apparatus for the simultaneous sampling of small volumes of blood from different blood vessels at constant rates is described.

W. H. C. SHAW

302. Micro-titration of organic compounds. IV. A micro-burette with constant rate of discharge. W. Simon (Org. chem. Lab., E.T.H., Zurich, Switzerland). *Helv. Chim. Acta*, 1956, **39** (3), 883-888.—An automatic micro-burette is described and illustrated in which Hg flows under const. pressure through a fine thermostatically controlled capillary tube into the reservoir of the titration solution; this soln. is thus displaced at a const. rate. A servo-motor and relay permit the automatic opening and closing of the tap of the burette. The unit is useful in the automatic determination of apparent dissociation const. in non-aqueous media and can be used to titrate 10^{-6} equiv. J. P. STERN

303. The sonic gas analyser. A. E. Martin (Sir Howard Grubb, Parsons & Co. Ltd., Newcastle upon Tyne, England). *Nature*, 1956, **178**, 407-408.—The theory and principles of the sonic gas analyser are discussed. The advantages over some other types of instrument are (i) no correction for variation in pressure is necessary; (ii) temp. compensation is easily arranged; (iii) practically any mixture of gases can be dealt with; (iv) the time lag can be made negligible; (v) the analysis unit is intrinsically safe in explosive atmospheres; (vi) it is possible to calculate to within a few per cent. the sensitivity of the instrument, and therefore actual calibration is unnecessary in many cases. N. E.

304. A tested distillation apparatus for the micro-analytical determination of nitrogen by the Kjeldahl method. W. Schöninger and A. Haack (Microanal. Lab., Sandoz A.-G., Basel, Switzerland). *Mikrochim. Acta*, 1956, (9), 1369-1372.—A simple, easily manipulated distillation apparatus is described. The apparatus may be used whenever reaction products are to be collected in a small volume of distillate. C. A. SLATER

305. A new technique for paper chromatography. M. Potterat (Service Fédéral de l'Hygiène Publique, Berne, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (1), 66-71.—A new way of folding and cutting filter-paper and developing the chromatogram is described with the aid of drawings. This new technique of circular paper chromatography incorporates the modifications proposed by Matthias. It yields well-defined spots and gives results that may be reproduced within narrow limits. It has been successfully applied to the separation of sugars, amino acids, purines, etc., and to the identification of adulterants in foodstuffs. H. A. FISHER

306. A simple spotting-pipette for paper chromatography. K. Holzer (Inst. für org. u. pharm. Chemie, Univ. Graz, Austria). *Mikrochim. Acta*, 1956, (9), 1434.—A simple pipette for delivering spots of samples on to filter-paper comprises a capillary tube pulled out to a narrow jet at one end and bent at right angles. The capillary is graduated in 0.5 to 1-cm sections so that each mark is equivalent to 1 μ l; the pipette is of such a length that it will deliver up to 20 μ l. C. A. SLATER

307. A contribution to the technique of radial paper chromatography. H. Sulser (Lab. Eidg. Gesundheitsamtes, Bern, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (2), 149-152.—An improvement on descending circular paper chromatography (Ganguli, *Experientia*, 1956, XII, 38) is described, the principal feature of which is the use of semi-circular pieces of paper, instead of full circles. This made possible the use of much larger sheets, viz. 29 cm in diameter, instead of the previous 13 cm. Substances of widely divergent R_F values could thus be separated in one operation. Additional advantages are that standard air-tight boxes can be used and several sheets may be simultaneously run in the same box. A. TESSLER

308. Test of drugs by paper partition chromatography. IX. A direct quantitative determination of substances in paper-chromatographic spots by an electrophotometer. Atsuo Takahara and Shigeru Taniguchi (Osaka Municipal Higashi Citizen's Hospital, Sugiyama-cho, Higashi-ku, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (7), 873-877.—In a

method for mounting a paper-chromatographic spot for absorption measurement, the spot is placed between the photocell and the slit of a filter photometer, so that the beam passes uniformly through the spot. The overall transmission of the paper is markedly increased by impregnating it with liquid paraffin. Precise experimental conditions were examined by the use of aq. soln. of picric acid (500 to 8000 μ g per ml). K. SAITO

309. The permanent viscometer, a direct indicating, registering and also regulating capillary viscometer. O. Leib (Lab. de Fa. Dr. Kühlewein, Bad Wiesner, Germany). *Kolloidzshr.*, 1956, **145** (2), 126-131.—A description and evaluation is given of the permanent viscometer. The measurement of kinetic and dynamic viscosity by means of the instrument is also discussed and error limits are indicated. R. J. MAGEE

310. Newer apparatus for the viscometric determination of molecular weight. H. Umstätter (Bundesanstalt für mechanische u. chemische Materialprüfung, Berlin-Dahlem, Germany). *Kolloidzshr.*, 1956, **145** (2), 102-108.—Apparatus described includes two capillary viscometers, the free-flow viscometer, the structure viscometer and two rotation viscometers, the thixotrometer and rheometer. R. J. MAGEE

311. A new consistometer and a new type of electro-rotation viscometer. W. Heinz (Lab. Firma Gebr. Haake A.-G., Berlin u. Düsseldorf, Germany). *Kolloidzshr.*, 1956, **145** (2), 119-125.—A consistometer is described whose outer construction is similar to the Höppler consistometer. By means of a new type of measuring body, a capillary flow is produced through its movement in the substance. This permits absolute measurement and the measurement of the constants of pure substances. It is supposed that the substances show no essential time-dependence in their rheological behaviour. An extension of the theory for the case of 'n' capillaries is developed. A new type of rotation viscometer is also described which contains an arrangement for the production of a more suitable velocity of rotation. The viscosity-dependent moment of rotation is measured electrically on a rotating axle in the viscous substance. The measurement of flow limit is also possible. R. J. MAGEE

312. Improvements relating to viscosity measurements [particularly on thixotropic or pseudo-thixotropic materials]. National Research Development Corp. (Inventor: Donald McKenzie). Brit. Pat. 751,958; Date appl. 12.1.52.—An apparatus for determining a representative value for η for a thixotropic viscous composition comprises a receiver for the composition and a body (perforated disc) arranged to fall through the composition combined with mechanical means (e.g., a helical spring) for applying a force which varies in known manner to restrain the fall of the body. The relative movement of the falling body with respect to its time of fall is recorded graphically. J. M. JACOBS

313. Simple gas-analysis apparatus for determining carbon dioxide and monoxide, oxygen, and nitrogen in a few cubic centimetres of gas mixture. M. Rossberg (Inst. für phys. Chem. Univ. Hamburg, Germany). *BrennstChmie*, 1956, **37** (7-8), 121-122.—The gas is driven by Töpler pumps through a glass apparatus consisting of four successive sections isolatable by taps, the whole being initially

evacuated to ≈ 0.1 mm (Hg). The first section carries a capillary U-tube in which CO_2 can be frozen out by liquid air, and a mercury manometer. Section 2 comprises a small furnace containing I_2O_5 in which CO is burned at 220° , followed by an absorber for I packed with silver wool. Section 3 resembles section 1 and is used for freezing and determining the CO_2 produced in section 2. Section 4 is connected to a furnace packed with granular C in which O is converted into CO at 1250° , its amount being determined from the resulting pressure rise. The residual gas, less the volume of CO, is N. The capacity of each section is determined with the manometer, Hg standing at a level fixed by an internal glass spur; the tube dimensions are such that the capacity of each is 2 to 4 cu. cm. Gas pressures in sections 3 and 4 are corrected by Boyle's law to what they would be if the gas were transferred to section 1. If H is to be determined, the temp. of the I_2O_5 is lowered to between 180° and 190° and the gas is circulated through it by a subsidiary mercury vapour pump. The H is eventually oxidised by CuO. The precision is within $\pm 0.4\%$. An analysis takes ≈ 25 min.

A. R. PEARSON

314. Determination of particle size with a simple recording sedimentation balance. J. G. Rabatin and R. H. Gale (Chem. Prod. Plant, Gen. Elect. Co., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1314-1316.—The balance records the weight of particles settling on a pan which is carried on a spring and suspended in the dispersing medium. Extension of the spring moves a shutter in the path of a light beam falling on a photocell. Change in weight is proportional to change in photo-current and is shown on a Speedomax recorder. Particle size may be deduced from this curve. Good precision was attained for the measurement of particle size from 2 to $30\ \mu$ and good agreement was obtained with measurements made with the Andreasen pipette.

P. T. BEALE

315. Apparatus for use in sampling particulate clouds such as airborne dust. National Research Development Corp. (Inventors: H. Lloyd and G. E. Winder). Brit. Pat. 755,522; Date appl. 26.8.53.—The dust sampler (for detecting particles within a particular size-range and producing a single sample from which the average concn. of such particles present in the atm. over a considerable length of time may be ascertained) comprises a slowly rotating (1 revolution in ≈ 30 min.), continuously-acting pump (e.g., a liquid-sealed rotary pump having a rotor partly immersed in water and provided with vanes so shaped that the rate of displacement of gas is proportional to the rate of rotation of the rotor), through which passes a continuous gaseous stream flowing at a predetermined rate for a predetermined length of time, and a filter through which the stream passes before entering the pump. The approach of the gas stream to the filter is in the upward direction and at a low rate through a throat such that particles below a given size are carried along to the filter by the gaseous stream before entering the pump, whilst the larger particles are pptd. before contacting the filter-paper on which the smaller particles form a stain.

J. M. JACOBS

Optical

316. Quantitative analysis of powder mixtures with an X-ray diffractometer equipped with Geiger counter. I. Sources of error. Yuji Hagino, Genzo Hashizume and Shiro Takashima (Cent. Res. Inst. of Ind. of Hyogo Prefecture, Kamitezaki-cho, Sumaku, Kobe). *Japan Analyst*, 1956, **5** (2), 91-95.—Sources of error in the determination of the mixing ratio by means of an X-ray diffractometer were studied with a mixture of NaCl and KCl. The greatest source appears to be the heterogeneity of the mixture and the difference in grain size. A wider slit favours an accurate measurement of the peak, but brings about a more diffused peak for each crystal face. It is therefore recommended that the intensity should be calculated not from the peak height but from the area. When the mean value of several measurements with different samples is taken for the estimation in place of a simple measurement, the relative error decreases by half.

II. Determination of the mixing ratio of some white pigments. Genzo Hashizume and Yuji Hagino. *Ibid.*, 1956, **5** (4), 205-209. The mixing ratio of binary mixtures of rutile, anatase, CaCO_3 and ZnO in paints and poly(vinyl chloride) sheets was studied with the same apparatus (Cu K_α line). It was again made clear that the error is greater when the sample contains larger grains such as calcite powder.

III. Quantitative analysis of products of double decomposition between potassium chloride and sodium sulphate. Genzo Hashizume and Yuji Hagino. *Ibid.*, 1956, **5** (4), 209-211.—The phase equilibrium of KCl, Na_2SO_4 , K_2SO_4 , NaCl and $\text{K}_2\text{Na}(\text{SO}_4)_2$ (glaserite) was studied with the same apparatus (Part I). It was empirically confirmed for this system that the additive law holds for the sum of two coinciding peaks. The composition of glaserite changes with different mixing ratios of the starting material, K_2SO_4 and Na_2SO_4 .

K. SAITO

317. Some applications of the micro-volume technique to emission spectrochemistry and metallurgy. J. K. Hurwitz (Dept. of Mines and Technical Surveys, Ottawa, Ontario, Canada). *Appl. Spectroscopy*, 1956, **10** (3), 124-128.—In this technique the specimen is moved over a spark discharge from a 30° -pointed silver electrode, which gives a crater of between 0.3 and 1.0 mm radius, depending on the melting point of the sample. The photographic plate is moved at the same time so that each point in the spectral line is a measure of the composition of a small volume in the surface of the specimen. A working formula is deduced for the conversion of the apparent concentration shown by each point in a line to the actual composition of the sample. Examples are given of the application of the technique to the analysis of segregates and to the measurement of diffusion in metals. The use of a moving specimen has also been found to eliminate sparking-off effects in zinc-base alloys.

P. T. BEALE

318. Spectrochemical analysis by means of the d.c. carbon arc. N. W. H. Addink, with J. A. M. Dikhoff, C. Schipper, A. Witmer and T. Groot (Philips Res. Lab., Eindhoven, Netherlands). *Appl. Spectroscopy*, 1956, **10** (3), 128-137.—An approx. constant temp. arc is achieved in this method by adding an excess of carbon powder and by loading certain pure materials, together with the 5-mg sample, into the anode crater to produce

controlled vaporisation. Complete volatilisation of the sample takes place in 6 to 8 min. with a current of 10 to 12 amp. Relative intensities of the analysis lines are deduced by comparison with a standard iron arc source and these are converted to actual concn. by the application of a factor K . Values of K have been deduced empirically and those for the major lines of 38 elements are given. The method may be applied to any type of sample and the determination of any constituent is claimed to be accurate within $\pm 10\%$ of the actual content.

P. T. BEALE

319. Photo-electric arrangement for quantitative spectrometric analysis. I. V. Podmoshenskii and L. D. Kondrasheva. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1955, **19** (1), 36-38; *Ref. Zhur., Khim.*, 1956, Abstr. No. 7059.—In order to register the intensity of spectrum lines, antimony-caesium photoelements in Uviol containers were employed. To obtain spectra in the range 2000 to 5000 Å, a diffraction grating was used with a radius of curvature 2 m, 1200 lines per mm, and dispersion 4 Å per mm. Discharge of the condenser accumulating the charge is intensified by using a valve electrometer and is measured by means of a valve voltmeter. The current is stabilised by an electronic stabiliser. The spectrum is created by an electronically controlled generator. The error due to the apparatus is not more than 1%. In the analysis of slightly alloyed steels the error does not exceed that in the usual photographic method.

R. LORD

320. Nature of the influence of sparking in the spectral analysis of metallic alloys. E. S. Kudelya. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1955, **19** (1), 136-138; *Ref. Zhur., Khim.*, 1956, Abstr. No. 10,058.—Distortion effect is explained as being the result of two processes: selective oxidation of elements and difference in diffusion rate from the bottom of the sample to the surface. Experimentally this theory is supported by means of obtaining distortion curves through freezing the samples in liquid oxygen or by preliminary heating to 1200°. To lessen and remove the distortion effect the following are recommended—(i) use of powerful impulsory sources with localisation of discharge; (ii) heating the samples to temperatures in the region of the melting point of the metal with the aid of induction heaters. This method combined with a method worked out previously (*Ref. Zhur., Phys.*, 1955, Abstr. No. 10,205) cuts down an extensive range of spectral standards.

R. LORD

321. Importance of evaporation equilibrium in the use of carbon disc- and rod-electrodes in the spectrochemical analysis of solutions. A. G. Herrmann (Metal Res. Works, German Acad. Sci., Berlin). *Chem. Tech., Berlin*, 1956, **8** (3), 132-134.—Comparative tests show that, in the arc spectrochemical analysis of solutions, the rotating small carbon disc-electrode of Schiebe and Rivas (*Angew. Chem.*, 1936, **49**, 443) gives much better results than the usual thin carbon rod-electrode. With the disc electrode both reliable qualitative and accurate quantitative results can be obtained, even when several elements of different b.p. are present in the solution. The improved results are due to the ability of the disc electrode to establish a stable evaporation equilibrium in the arc area (within 2 min.), and when several elements of different b.p. are present (Hg, As, Mn, Th and Mo) the fractionating effect experienced with the rod electrode is obviated, thereby enabling a simul-

taneous analysis of all the elements to be effected. Traces of the foreign metal in a solution of a metal salt can be detected with the disc electrode in a relatively short time. The advantages are illustrated by comparative analyses of mixtures of elements.

H. L. WHITEHEAD

322. Frequency-linear drive for spectrographic recorder. W. E. Deeds (Univ. of Tennessee, Knoxville, U.S.A.). *Rev. Sci. Instrum.*, 1956, **27** (7), 543-544.—Radiation passing through the spectrometer is also passed through a Fabry-Perot interferometer. The transmitted radiation, which exhibits intensity maxima at equal frequency intervals, is detected, and the a.c. signal is amplified and made to drive a synchronous motor of the recorder.

G. SKIRROW

323. Errors introduced by the use of unbalanced solvent media in differential spectrophotometric measurements. G. M. Junejo and A. L. Glenn (The School of Pharmacy, University of London). *Chem. & Ind.*, 1956, (31), 813-814.—The "Δε method" recently described by Aulin-Erdtman (*cf. Chem. & Ind.*, 1955, (21), 581) is reviewed and it is suggested that the errors of this method will not exceed those of normal spectrophotometric technique if—(i) the acid or alkali concentration is $< 0.1 N$; (ii) the 'added' absorption of the two spectra is < 0.86 ; and (iii) the absorbing impurities are non-fluorescent.

E. G. CUMMINS

324. Transistor-amplifier units for absorptiometry. P. W. Perryman and D. H. Richards (Southend-on-Sea Hosp., Rochford, Essex, England). *J. Clin. Path.*, 1956, **9** (3), 273-276.—Two types of amplifier units, with transistors, are described; these enable narrow-band filters to be used with simple types of photo-electric absorptiometers.

H. F. W. KIRKPATRICK

325. Quantitative infra-red absorption spectroscopy in water solution. W. J. Potts, jun., and N. Wright (Dow Chem. Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1255-1261.—A useful spectral range between 6.5 and 10 μ is obtained by the use of a very thin cell with barium fluoride windows. The method of construction of such a cell, with a path length of 0.027 mm, is described. The low energy resulting from the water absorption is offset by using a monochromator entrance slit that is wider than normal. Applications to the quant. estimation of water-soluble organic salts and glycols are described. A spectrum of centrifuged blood plasma indicates a possible application to biological preparations.

P. T. BEALE

326. The infra-red spectrometer as a non-dispersive instrument. R. Burt and G. J. Minkoff (Imperial Coll., London). *J. Sci. Instrum.*, 1956, **33** (7), 283.—The paper describes modifications made to a double-beam infra-red spectrometer enabling it to be used as a non-dispersive gas analyser.

G. SKIRROW

327. Sodium vapour lamp Raman excitation source for the study of coloured compounds. F. T. King and E. R. Lippincott (Univ. Maryland, College Park, U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (8), 661-662.—The Raman spectra of compounds which are both coloured and photosensitive have been obtained by using high-intensity sodium lamps in the light source. The source-unit consists of four sodium vapour lamps mounted in a cylindrical metal container, the Raman tube with

water-cooled filter jacket being mounted, as usual, in the centre of the unit. Liquid filters eliminate radiation of wavelength $< 568 \text{ m}\mu$ and between 600 and 700 $\text{m}\mu$. The Raman spectra of $\text{Fe}(\text{CO})_5$ and diazocyclopentadiene, obtained in this manner, are tabulated.

B. S. COOPER

328. Short-light-path absorption cell for routine colorimetry. D. C. Udy (Agric. Res. Ser., U.S. Dept. of Agric., Pullman, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (8), 1360.—A method of constructing a cell with a 0.007-in. liquid path is described. Formation of air bubbles when filling the cell is prevented by a preliminary flushing with a 0.5% soln. of octan-2-ol.

P. T. BEALE

329. Oxyhaemometer—a photo-electric apparatus for studying anaemia and the continuous determination of the degree of saturation of blood with oxygen. M. S. Shipalov. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1955, **19** (2), 154-155; *Ref. Zhur., Khim.*, 1956, Abstr. No. 13,295.—The apparatus, which is fixed to the helix of a patient's ear, measures the absorption of light at 650 $\text{m}\mu$ passing through the tissue of the ear. The current generated by a photoelement is registered by a galvanometer graduated in percentage saturation of the blood by oxygen.

G. S. SMITH

330. Some applications of the use of the reflectance photodensitometer to spot-test analysis. C. W. Ayers (Birmingham Univ., England). *Mikrochim. Acta*, 1956, (9), 1333-1349 (in English).—A quantitative estimation of substances present in test solutions has been made with the reflectance photodensitometer to measure the colour developed in spot tests. The relationship between instrument reading and concentration of test substance and the best method of obtaining uniform colours are discussed. The technique was applied to the determination of metals as sulphides, of polyamides in blends with other fibres, and of amines and amino acids with ninhydrin. Only 5 to 10 μl of soln. is required for the analysis. From 5 to 0.2 μg of metal ions, 100 to 5 μg of polyamide, and 1 to 0.05 micro-equiv. of amino nitrogen can be determined.

C. A. SLATER

331. Refractometer for liquids and gases. LKB-Produkter Fabriksaktiebolag. Brit. Pat. 750,723; Date appl. 22.3.54. (Date appl. Sweden, 18.4.53).—The instrument comprises a special cell, a collimator, etc. The cell comprises a compartment for the medium to be examined which is separated by a plane wall from a reference medium compartment and by another wall, perpendicular to the first wall, from an outer medium, e.g., the air or the liquid in a thermostat. The compartment for the reference medium (which may be a fluid or glass) also has an outer wall, which is perpendicular to the first-mentioned wall and consequently parallel with the outer wall of the compartment for the liquid to be measured. The cell is arranged in the refractometer so that light from a collimator enters the reference medium through its outer wall, passes thence through the first-mentioned wall into the liquid being examined, and finally leaves the cell through the wall parallel to the entrance wall. The cell is mounted on a turntable so that it is rotatable about an axis parallel with the above-mentioned three walls and perpendicular to the axis of light entering the cell, whereby the entrance angle for the light is continuously variable and thus a continuously variable sensitivity of the cell is obtained. The turntable carries a scale indicating

the values of the entrance angle α (the angle between the incident light and the normal to the cell wall) which satisfy the equation— $\tan 2\alpha \sin 2\alpha = 4n^2$, where n is the refractive index of a particular reference medium, since the use of this entrance angle enables an unusually wide range of linear response to be obtained. The arrangement for receiving light deflected in the cell is combined with means for measuring the light deflection in the cell or a function of that deflection.

J. M. JACOBS

332. Improvements relating to refractometric cells [comprising differential-prismatic cells]. LKB-Produkter Fabriksaktiebolag. Brit. Pat. 750,727; Date appl. 2.4.54. (Date appl. Sweden, 16.10.53).—The differential-prismatic cell comprises two mutually parallel outer walls adapted to be disposed perpendicularly to the light path in a refractometer, and inner walls which meet the outer walls along mutually parallel straight lines. At least one pair of the inner walls is mutually parallel and forms acute angles with the outer walls. The walls are so arranged that in use of the cell one medium, in every section perpendicular to the mutually parallel straight lines, is delimited partly by the two outer walls and partly by at least one pair of mutually parallel inner walls, and the other medium in a similar section is delimited by the inner walls and the remaining parts of the outer walls. If the cell is placed in the path of parallel light from a collimator, it gives rise to two light-beams which form a certain angle with each other. On focusing these beams, two images of the collimator slit are obtained, the mutual angular separation of which is proportional to the refractive-index difference.

J. M. JACOBS

Thermal

333. Apparatus for the determination of melting points and boiling points. W. S. Owen and W. M. Reid (Tech. Coll., Coventry, England). *Mikrochim. Acta*, 1956, (9), 1373-1376 (in English).—A simple apparatus which makes use of an aluminium block heated by means of a micro-burner is described.

C. A. SLATER

334. Continuous measurement of deuterium concentration in hydrogen by means of thermal conductivity. M. Silvestri and N. Adorni (CISE, via Procaccini 1, Milan, Italy). *Rev. Sci. Instrum.*, 1956, **27** (6), 388-391.—Concentrations of deuterium in hydrogen of up to 2.5% can be measured with an accuracy of 1 in 10,000 by means of a thermal conductivity unit. Details of apparatus are described.

G. SKIRROW

Electrical

335. The cleaning of gilded cathodes. C. Duval (École Nat. Sup. de Chimie, 11 rue Pierre Curie, Paris, France). *Mikrochim. Acta*, 1956, (9), 1433.—A study has been made of the methods used for cleaning gold or gilded platinum cathodes that have been employed in the electrolytic determination of Hg. The removal of the Hg by heating in a naked Bunsen flame is not to be recommended since this produces a deformation of the electrode. It is better to heat the electrode either in an air oven or, preferably, in a thermostatically controlled electric furnace at 261°, at which temperature the cathode is completely cleaned.

C. A. SLATER

336. Two new Czech polarographs. B. Petzelt and L. Šerák (Lab. přístroje, n.p. und Polarographic Inst. Czech. Acad. Sci. Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (3), 783-785.—Two new polarographs of conventional type, soon to be commercially available, are described. The first is a small portable instrument, the curves being drawn manually on translucent paper by following the galvanometer spot. The second is a photographic instrument designed to meet all the needs of polarographic analysis. It combines accuracy and reliability with simplicity of control.

P. S. STROSS

337. Electrolysis vessel for polarographic series analyses. H. G. Nieter (Lab. of VEB, Mansfeld Hütten-Kombinat "Wilhelm Pieck," Eisleben, Germany). *Chem. Tech., Berlin*, 1956, **8** (2), 80.—A full description is given of the construction and operation of an improved and simple electrolysis vessel developed for rapid polarographic series analyses of soln. The apparatus is also useful for estimations of Cu, Pb, Zn and Ni. The electrolytic cell is fitted into a bath provided with means for heating to const. temp. and is provided with connections to the supply of test soln., to the mercury anode and to N for de-aerating the cell. This enables successive soln. to be simply and rapidly treated in the cell without any disconnections. Before the introduction of each soln., water is run through the cell to wash it out. By the use of two cells, one test soln. can be heated to the requisite temp. and be flushed with N while another test soln. is being analysed in the second cell.

H. L. WHITEHEAD

338. Hydrogen-ion concentration measuring apparatus. Foxboro Co. Brit. Pat. 753,074; Date appl. 20.5.54.—The soln., the pH of which is to be measured, flows through a stainless-steel pipe acting as contact electrode. A measurement half-cell (e.g., a quinhydrone glass electrode), a reference half-cell (e.g., a calomel cell) and a temp. sensor comprising a thermocouple and two sensitive resistive elements (e.g., nickel thermometer bulbs) are inserted through an opening in the tube wall. Connection is made to the measurement half-cell through the inner conductor of a coaxial cable,

the outer conductor of which acts as a shield against stray electrical fields. Connection is made to the soln. through the pipe and a lead which is returned to a common system ground circuit. Because of the electrochemical cell activity, voltages will be developed between the common ground and each of the half-cell terminals. The difference between these voltages will be equal to the difference in potential between the half-cell terminals, which is a measure of pH for any given temp. of the soln. being tested. Owing to the high internal cell resistance this voltage difference is measured by means of a potential comparison arrangement, with an amplifier acting as an impedance converter and current amplifier.

J. M. JACOBS

339. High-frequency titration. Q-metric analytical method. Yu. Yu. Samitov (V.I.Ul'yanov-Lenin Kazan State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (2), 149-158.—Apparatus for a modification of the Q-metric method is described. Characteristic curves (current-concn.) for the soln. studied show a max. which satisfies the semi-empirical equation $\lambda C = 23.29 \frac{D}{\Lambda_0}$, where λ is the wavelength in cm, C is the mol. concn. of the electrolyte at the max., D is the dielectric const. of the solvent, and Λ_0 is the limiting equivalent conductivity of the electrolyte (KCl, NaCl, HCl or other univalent electrolyte).

G. S. SMITH

340. End-point calculation in conductimetric and photometric titrations. E. Grunwald (Weizmann Inst. Sci., Rehovoth, Israel). *Anal. Chem.*, 1956, **28** (7), 1112-1116.—The value of conductimetric or photometric titrations when potentiometric methods are impracticable is tested. Details are given of the theory and practice of a method of end-point determination in which the non-linear part of the titration curve near the end-point is used, thus minimising end-point errors due to variations in equivalent conductivities, deviations from Beer's law, and systematic experimental divergencies, and reducing the normal error of 10% to one of 0.5%. The conductivity K is plotted against ϵ , the ratio of the equivalents of titrant to those of substrate. No other data are required.

E. G. CUMMINS

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ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	m μ g
aqueous	aq.	millimolar	mM
atmospher-e, -ic.	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α
coefficient	coeff.	ounce	oz
concentrated	conc.	parts per million	p.p.m.
concentration	concn.	per cent.	%
constant	const.	per cent. (wt. in wt.)	% (w/w)
corrected	(corr.)	per cent. (wt. in vol.)	% (w/v)
crystalline.	} cryst.	per cent. (vol. in vol.)	% (v/v)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute.		qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n_D^{20}
electromotive force	e.m.f.	relative band speed	R_F
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{1/2}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_D^{20}$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μ g (not γ)	volt	V
microlitre	μ l	volume	vol.
micromole	μ mole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	\nlessgtr	not less than	\nlessgtr
is proportional to	\propto	of the order of, approximately \approx	

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II}, Mo^V. Substances in the ionic state are represented by Na⁺, Fe²⁺, Fe³⁺, etc., for cations and by Cl⁻, SO₄²⁻, PO₄³⁻, etc., for anions.

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